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CHEMILUMINESCENT REACTIVE HYDROCARBON ANALYZER FOR MOBILE SOURCES

A. Fontijn, et al

AeroChem Research Laboratories, Incorporated

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CHEMILUMINESCENT REACTIVE HYDROCARBON ANALYZER FOR MOBILE SOURCES

by

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June 1975

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ABSTRACT

A chemiluminescence method for measuring total reactivity of hydrocarbon (HC) mixtures has been developed and a prototype analyzer based on this method has been built. The difference between the $OH(A^2\Sigma^+ - X^2\Pi)$ emission intensities at 308.9 and 312.2 nm from O-atom/hydrocarbon reactions near 1 Torr is measured. For C_2H_4 $I_{308.9} > I_{312.2}$, for C_2H_2 $I_{308.9} \approx I_{312.2}$. The other hydrocarbons tested yield the same spectral distributions as C_2H_4; CH_4 yields no emission. Two PMTs are used for 308.9 and 312.2 nm measurement respectively. When the apparatus is zeroed, the difference in signal from the two PMTs is insensitive to C_2H_2. The relative response to the individual reactive HC species can be set to give good agreement with reactivity ratings. The response to HC mixtures is additive. A limit of sensitivity of ≈ 0.05 ppm C_2H_4-equivalent HC and a linear response to individual HCs to 2500 ppm is obtained; greater sensitivity appears feasible. CO, CO_2, SO_2, CH_4, C_2H_2 and NO_x do not interfere with instrument response. A 1% change in $[O_2]$ causes < 1% change in signal; 3% H_2O causes a 12% decrease.

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CONTENTS

Sections		Page
I	Conclusions	1
II	Recommendations	2
III	Specifications of Prototype Instrument	3
IV	Introduction	4
Part I:	Feasibility Study by Arthur Fontijn and Roy Ellison	7
V	Survey Study	8
	A. Approach	8
	B. Experimental	10
	C. Investigation of Emissions Other than $OH(A^2\Sigma-X^2\Pi)$	13
	1. $CN(B^2\Sigma-X^2\Sigma)$	13
	2. $NO(\beta,\gamma)$ and CO Cameron Emissions	14
	D. $OH(A^2\Sigma-X^2\Pi)$ from O-Atom Reactions	15
	1. Spectral Distribution and Intensities	15
	2. Reaction Kinetics and Kinetic Spectroscopy	19
VI	The Chemiluminescence Hydrocarbon Analyzer Test Apparatus Experiments	22
	A. Experimental	22
	1. Gas Handling System and Flow Conditions	22
	2. Radiation Measurement	24
	3. Electronics	24
	B. Results and Discussion	26
	1. Acetylene Zero	26
	2. Response to Individual Hydrocarbon Species	26
	3. Interference by Other Species Present in Mobile Engine Exhausts; Influence of Variable % O_2	30
	4. Measurements with Other Reagent Gas Compositions	34
	5. Hydrocarbon Mixtures	35
Part II:	Manual for Prototype Analyzer by Hermann N. Volltrauer and Arthur Fontijn	39
VII	Technical Description	40

		Page
VII	A. Gas Handling System	40
	1. Sample Gas System	40
	2. Reagent Gas System	40
	3. Reactor and Vacuum Pump	46
	B. Light Detection System	47
	C. Electronics	47
	1. Measuring Electronics	47
	2. Microwave Power Supply	49
VIII	Operating Instructions	52
	A. Descriptions of Panels and Controls	52
	1. Front Panel	52
	2. Rear Panel	53
	B. Installation and Set-Up	53
	C. Operation	54
	D. Calibration	55
IX	Maintenance and Troubleshooting	57
	A. Planned Maintenance	57
	B. Disassembly and Reassembly	57
	1. Cabinet	57
	2. PMT Housing	58
	3. Sample Inlet Nozzle	59
	4. Reactor	59
	5. Vycor Discharge Tube	60
	6. Valves	60
	7. Microwave Power Supply	60
	C. Troubleshooting	61
	D. Signal Processor Board Adjustments	63
	E. Shipping	64
X	Tests	65
	A. Reagent Gas Purification Traps	65
	B. Collimators	65
	C. Flow Rates	65
	D. Nozzle Distance and Microwave Power	66
	E. Linearity and Limit-of-Sensitivity	66
	F. Response Ratios	66
XI	References	69
XII	Inventions and Publications	72
APPENDIX A:	List of Manufacturers of Parts Used in Prototype Instrument	73

FIGURES

No.		Page
1	Schematic of Conventional Fast Flow Reactor.	11
2	$OH(A^2\Sigma-X^2\Pi)$ Emission from the O/C_2H_4 and O/C_2H_2 Reaction.	18
3	$I_{308.9}$ versus C_2H_4 Flow.	18
4	Influence of O_2 on 308.9 nm Intensities from O/C_2H_4 and O/C_2H_2.	21
5	The Chemiluminescence Hydrocarbon Analyzer Test Apparatus.	23
6	Diagram of Electronics for the Hydrocarbon Analyzer Test Apparatus.	25
7	Exponential Dilution Plot for Propadiene.	27
8	Response versus Concentration of Ethylene and n-Butane with He/9% O_2 Reagent Gas.	28
9	Absence of Interference by Methane.	31
10	Absence of Interference of NO_x with n-Butane Measurement.	32
11	Effect of O_2 in Sample Gas on $\Delta I_{308.9}$ Response for 12.5 ppm C_2H_4.	33
12	Response versus Concentration of Ethylene and n-Butane with Undiluted O_2 Reagent Gas.	34
13	Comparison of Response of Ethylene and n-Butane to that of Their Mixture at the Same Individual Concentrations.	37
14	Front View.	41
15	Rear View.	42
16	View with Side Panel Folded Down.	43
17	Top Inside View.	44
18	Side View with Cover Off.	45
19	Signal Processor Circuit	48
20	Microwave Power Supply Wiring.	50
21	Chassis Wiring.	62
22	Response of Ethylene, Iso-Octane and Benzene as a Function of Nozzle Distance and Microwave Power.	67

TABLES

No.		Page
1	Relative Chemiluminescence Signal Intensities of Class V, IV, III, and I Hydrocarbons, at High Hydrocarbon Concentration in Survey Apparatus	17
2	Effect of Nozzle Distance on $\Delta I_{308.9}$ for He/9% O_2 Discharge Gas and 1250 ppm Hydrocarbon	27
3	Relative Chemiluminescence Signal Intensities of Class V, IV, III, and I Hydrocarbons Obtained at 1.5×10^{-2} sec Reaction Time for He/9% O_2 Discharge Gas	29
4	Concentration Ranges of Hydrocarbons (in ppm) for which Interference was Investigated at the Indicated Interference Gas Concentration	31
5	Changes in $\Delta I_{308.9}$ from 125 ppm C_2H_4 and n-C_4H_{10} as a Function of O-Atom Concentration for He/9% O_2 Reagent	36
6	Prototype Analyzer Relative Chemiluminescence Signal Intensities of Class V, IV, III, and I Hydrocarbons at Microwave Power Levels of 20% (A) and 30% (B) of Full Scale	68

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We thank P.J. Howard for assembling the prototype instrument. J. Rose assisted with some of the survey experiments.

SECTION I

CONCLUSIONS

This work demonstrates that instruments based on the $\Delta I_{308.9}$ method here developed give readings of total hydrocarbon reactivity closely approximating those which can be obtained by measuring each hydrocarbon individually with a gas chromatograph and multiplying its concentration with the appropriate reactivity factor. Since a $\Delta I_{308.9}$ instrument, at continous flow, gives a continuous direct reading, far less time and effort is involved in using apparatus based on this method.

In this work emphasis was placed on approaching the Dimitriades reactivity scale. However, the response to the individual reactive hydrocarbons can be adjusted by varying (1) the relative sample and reagent gas flow rates, (2) the O-atom concentration (by varying the microwave discharge power) or (3) the reaction time (by adjusting the hydrocarbon nozzle to PMT distance and/or changing the average gas velocity). Such adjustment to the desired reactivity scale is possible due to the differences in the rate coefficients of the reactions of O atoms with the different hydrocarbons as well as the hydrocarbon fragments formed in the initial O atom attack. Thus a response where all reactive hydrocarbons are weighted roughly equal would seem possible. Such an instrument setting becomes of interest when rural smog situations have to be considered.

By making the $I_{308.9}/I_{312.2}$ ratio unity for reactive hydrocarbons, acetylene can in principle also be measured. This would require minor modifications of the prototype instrument. However, the O-atom/acetylene reaction has many strong emission features other than those used in the present instrument. Some of those emissions appear much more suitable for an instrument built specifically for acetylene monitoring.

SECTION II

RECOMMENDATIONS

The prototype instrument delivered is suitable for measurement of ethylene equivalent hydrocarbon concentrations from 0.05 to 2500 ppm. This range is adequate for mobile source work. In the future a monitor for ambient reactive hydrocarbons, i.e. a monitor of greater sensitivity may be required. The same basic principle as used for the present instrument can very likely be employed to yield an instrument with a sensitivity on the order of 10 ppb or better by making the following modifications:

1. Using lenses to increase the light-gathering capability of the photomultiplier tubes (PMTs) monitoring the reaction zone.

2. Using quartz (instead of Pyrex) viewing ports and PMT envelopes.

3. Using a larger reactor to cover the entire PMT face.

4. Optimizing the reactor design using information obtained from the present instrument and the literature on O-atom/hydrocarbon reactions.

5. Optimizing filter and collimator selection by a careful analysis of the O/hydrocarbon and background spectra near 310 nm.

Item 5 may decrease the background signal relative to the sample signal while the others are expected to increase both signals proportionally. Items 1, 2 and 3 can result in a factor of 10 to 15 more light reaching the PMTs. Since the noise in the background (the sensitivity limiting factor) is mainly due to the statistical nature of the signal, it will increase approximately as the square root of the signal. A factor of 10 to 15 more signal can therefore result in an increase of 3 to 4 in sensitivity. Items 4 and 5 will undoubtedly result in some improvement in sensitivity but the amount cannot be quantitatively assessed.

SECTION III

SPECIFICATIONS OF PROTOTYPE INSTRUMENT

SENSITIVITY (ethylene equivalent)	0.05 ppm (S/N = 2)
USEFUL CONCENTRATION RANGE	0.05 to 2500 ppm
FLOW RATES: SAMPLE REAGENT	1 ml.atm sec^{-1} 3 ml.atm sec^{-1}
PRESSURE	1.6 Torr
OPERATING RANGES	Eight full scale ranges: 1, 2.5, 10, 25, 100, 250, 1000, 2500 ppm
TIME CONSTANTS	0.1, 0.3, 1, 3, 10 sec.
LINEARITY	Linearized to within 3 % of full scale
TEMPERATURE	Operates at room temperature
READ OUT	15 cm analog meter on front panel with adjustable recorder output of 0-1 V
LINE VOLTAGE RANGE	105-125 V
POWER REQUIREMENTS (exclusive of vacuum pump)	115 V, 60 Hz, 400 W
EXTERNAL CONNECTIONS	A source of O_2 (10% in Ar) and a vacuum pump
VACUUM PUMP	150 l/min capacity, Welch Duo-Seal 1402B-01 or equivalent
SIZE	51 × 56 × 67 cm
WEIGHT	70 kg (150 lbs)

SECTION IV

INTRODUCTION

The formation of photochemical smogs requires both NO_x and organic pollutants, particularly hydrocarbons. However the ability of hydrocarbons to produce smogs varies greatly depending upon the rate coefficients of the many reactions involved (particularly attack by OH, O_3, and O).[1,2] For example, methane and acetylene are considered to be 'unreactive,' while ethylene and n-butane are 'reactive' hydrocarbons in terms of photochemical smog. However, severalfold higher n-butane than ethylene concentrations are required to produce similar atmospheric effects. Current U.S. hydrocarbon standards are based on total non-methane hydrocarbons, the measurement of which requires several steps, e.g. a flame ionization total hydrocarbon analyzer in combination with an infrared methane monitor or a gas chromatographic methane separator.[3] Alternatively a complete gas chromatographic analysis gives detailed information but is very time consuming. There is, accordingly a need, especially in mobile engine exhaust monitoring, for a measurement method that gives an indication of total hydrocarbon reactivity, i.e., gives the sum of the concentrations of each hydrocarbon species multiplied by an individual or group reactivity factor. Since the reactivity of hydrocarbons differs with respect to several parameters, e.g. butane contributes more heavily in late or downwind than in early smog situations, any hydrocarbon reactivity scale is of necessity somewhat arbitrary (compare Ref. 4); nonetheless a meaningful measurement technique should be approachable. The present work was undertaken to establish such a technique.

In Part I an initial survey study (Section V) of chemiluminescence in reactions of hydrocarbons with O and N atoms and mixtures thereof suggested one suitable method, i.e. the difference in $OH(A^2\Sigma - X^2\Pi)$ intensities, from O-atom reactions, at 308.9 nm and 312.2 nm. This work was followed by an exten-

---

1. Niki, H., Daby, E.E. and Weinstock, B., "Mechanisms of Smog Reactions," in Photochemical Smog and Ozone Reactions, Advances in Chemistry Series 113, American Chemical Society, Washington, DC, 1972, p. 16-57.

2. Leighton, P.A., Photochemistry of Air Pollution, Academic Press, New York, 1961.

3. Coloff, S.G., Cooke, M., Drago, R.J. and Sleva, S.F., "Ambient Air Monitoring of Gaseous Pollutants," American Laboratory, July 1973, 10-22.

4. Proceedings of the Solvent Reactivity Conference, EPA-650/3-74-010, November 1974.

sive feasibility study of this "$\Delta I_{308.9}$" technique (Section VI). Since this study showed that this method gives OH intensities in reasonable proportion to the desired hydrocarbon reactivity ratings[5] and has the sensitivity required for mobile exhaust monitoring, the construction of a prototype instrument for delivery to EPA was undertaken. This instrument is discussed in Part 2.

---

5. Dimitriades, B., "The Concept of Reactivity and Its Possible Applications in Control," Ref. 4, p. 13.

PART I

FEASIBILITY STUDY

by

Arthur Fontijn

and

Roy Ellison

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SECTION V

SURVEY STUDY

A. Approach

The objective of our initial effort was to find a prominent emission feature resulting from a reaction of C_2H_4 that would not occur to a measurable degree with C_2H_2 under the same reaction and observation conditions. The ≈110-900 nm spectral region was investigated since it lends itself to study with common photomultiplier tubes (PMT), which is the most suitable type of detector for measurement of low light levels, i.e. measurement of emission from trace concentrations. Once such a feature was found we checked whether other reactive, i.e. photochemical smog reactive, hydrocarbons would also yield the same emission as C_2H_4.

In view of the available time and funds it was decided to concentrate on reactions of O and N atoms which, on the basis of our past experience and the literature, offered the best prospects for yielding a suitable emission feature.† The other alternatives considered are:

(i) O_3 Reactions. These can readily be handled at near atmospheric pressure which is an advantage in a practical instrument. The successful operation of the Nederbragt type detector (C_2H_4/O_3) for O_3 suggests that this would be a suitable approach for C_2H_4 measurement. In view of the fact that other olefins can be used to replace C_2H_4[6-8] this route might be a promising one for an olefin-specific detector. However, it is commonly thought that saturated hydrocarbons would not yield any emission with O_3. Since this has apparently not been explicitly investigated it may remain worthwhile to further explore O_3 reactions.

---

† C_2H_2 and C_2H_4 are the only two hydrocarbons whose chemiluminescence had extensively been studied in the past.

6. Finlayson, B.J., Pitts, J.N. and Akimoto, H., "Production of Vibrationally Excited OH in Chemiluminescent Ozone-Olefin Reactions," Chem. Phys. Lett. 12, 495-498 (1972).

7. Kummer, W.A., Pitts, J.N. and Steer, R.P., "Chemiluminescent Reactions of Ozone with Olefins and Sulfides," Env. Sci. Techn. 5, 1045-1047 (1971).

8. Hodgeson, J.A., McClenny, W.A. and Martin, B.E., "Environmental Protection Agency, Private communications 1973 and 1974.

(ii) OH Reactions. Little is known about chemiluminescence in OH reactions. Since OH is the major reactive compound in photochemical smog, its chemiluminescent reactions might well correlate with hydrocarbon reactivity. The study of such reactions remains of interest, but could be complicated by emission from O-atom reactions since OH radicals react rapidly with each other to produce O-atoms via[9-10]

$$OH + OH \rightarrow H_2O + O \qquad (1)$$

C_2H_2 is known not to produce chemiluminescence with OH.[11]

(iii) Halogen Atom Reactions. Very few chemiluminescent reactions of Cl, Br and I have ever been observed. F atoms, which are more difficult to handle than O or N atoms (but not prohibitively so), produce a number of chemiluminescent reactions.[12]

(iv) H-Atom Reactions. H-atom/hydrocarbon reactions are apparently not chemiluminescent.[11,13]

---

9. Wilson, W.E. Jr., "A Critical Review of the Gas-Phase Reaction Kinetics of the Hydroxyl Radical," J. Phys. Chem. Ref. Data 1, 535-573 (1972).

10. Del Greco, F.P. and Kaufman, F., "Lifetime and Reactions of OH Radicals in Discharge Flow Systems," Disc. Faraday Soc. 33, 128-138 (1962).

11. Bayes, K.D. and Jansson, R.E.W., "The Origin of Light Emission in the Atomic Hydrogen-Acetylene Flame," Proc. Roy. Soc. A282, 275-282 (1964).

12. Schatz, G. and Kaufman, M., "Chemiluminescence Excited by Atomic Fluorine," J. Phys. Chem. 76, 3586-3590 (1972).

13. Gaydon, A.G., The Spectroscopy of Flames, John Wiley, New York, 1957, p. 252.

B. Experimental

A Pyrex fast-flow reactor, Fig. 1, available from previous studies of hydrocarbon chemiluminescent reactions, e.g. Refs. 14, 15 was used. With a mechanical vacuum pump such reactors are suitable for O- and N-atom reaction studies involving pressures from about 0.5 to 20 Torr (1 Torr = 133.3 Pa). The reaction tube is 2.2 cm i.d. Carbon compounds are introduced via a traversable nozzle into a gas stream containing either O atoms, N atoms, or a mixture of the two. The resulting chemiluminescence was observed in a direction perpendicular to the flow, through a LiF window downstream from the nozzle. The nozzle is adjustable to allow variation of reaction time, t; under otherwise steady flow conditions t is proportional to the nozzle to (observation) window distance. The effect of O_2 addition was studied by adding O_2 through an 'additive gas' inlet.

Atomic O was produced either by passing O_2 or mixtures of O_2 and Ar or He through a microwave discharge (2450 MHz) or, as shown in Fig. 1, but only occasionally used in this study, by passing N_2 (or N_2 + He or Ar) through the discharge, followed by titration of the resulting N atoms via

$$N + NO \rightarrow O + N_2 \qquad (2)$$

The advantages of the latter method are easy measurement of the O-atom concentration, [O], and production of O atoms free from O_2. The former method however yields larger quantities of O atoms. [O] in the case of the O_2 or O_2/Ar,He discharges was measured by comparison to the O/NO chemiluminescence intensity from over-titrated (excess NO) N/NO mixtures, as described by Fontijn and Lee.[16] In the N-atom studies no NO was added. To produce N/O mixtures, flows of NO less than those of N were added.

---

14. Fontijn, A., Ellison, R., Smith, W.H. and Hesser, J.E., "Chemiluminescent Emission of CO Fourth Positive Bands in Nitrogen Atom/Oxygen Atom/Reactive Carbon Compound Systems. Relation to Chemi-Ionization," J. Chem. Phys. 53, 2680-2687 (1970).

15. Fontijn, A. and Johnson, S.E., "Mechanism of CO Fourth Positive VUV Chemiluminescence in the Atomic Oxygen Reaction with Acetylene. Production of $C(^3P, ^1D)$," J. Chem. Phys. 59, 6193-6200 (1973).

16. Fontijn, A. and Lee, J., "Comparison of the Absolute Quantum Yields of the Gas-Phase O/NO Reaction and the Liquid-Phase Luminol Oxidation Chemiluminescence Standards," J. Opt. Soc. Am. 62, 1095-1098 (1972).

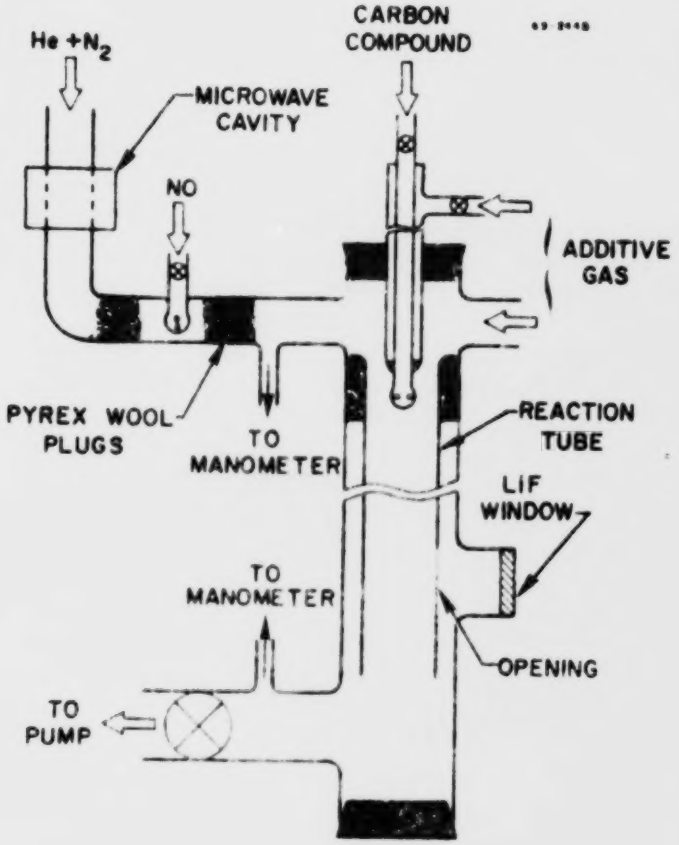

FIGURE 1. Schematic of conventional fast flow reactor.

All permanent gases used were c.p. grade or better. N_2, O_2, He and Ar, were passed through activated alumina (drying agent). The gaseous hydrocarbons were dried by passage through silica gel. NO was passed through silica gel and "Ascarite" NO_2 absorbent. The normally liquid hydrocarbons (Fisher certified grade toluene, n-heptane, iso-octane and benzene) were placed inside a flask submerged in a constant temperature bath. N_2 introduced through a fish tank bubbler passed through the flask: the hydrocarbon content of the saturated N_2 thus obtained was calculated using the data of Stull.[17] Flows were regulated with fine control needle

17. Stull, D.R., "Vapor Pressure of Pure Substances. Organic Compounds," Ind. Eng. Chem. 39, 517-540 (1947).

valves and measured via an equivalent oil flow in a partially submerged buret.[18] The lowest hydrocarbon flow rates measurable in this manner are $\approx 10^{-3}$ ml.atm sec^{-1}, while the practical total flow rates ranged from ≈ 1 to 10 ml.atm sec^{-1}. It follows that the lowest hydrocarbon concentrations that could be measured with this apparatus were in the range 100 to 1000 ppm, corresponding to the approximate upper limit of interest. Hence the apparatus used in the Section V experiments could not as such have been used for demonstrating feasibility, but only to indicate which features might be worth exploring further.† Pressures were measured with a Barocel electronic manometer calibrated against a U-tube oil manometer equipped with a micrometer depth gauge.

A Czerny-Turner type 0.5 m Minuteman Model 305-MHA monochromator with an f/6.9 aperture ratio, equipped with a Centronic C4242BA bialkali PMT mounted in a thermo-electrically cooled housing was used. In the studies below ≈190 nm a magnetic (photo) electron multiplier (MEM) detector with a Cu I photocathode was used instead of the 4242 tube and a pressure of $\approx 10^{-5}$ Torr was maintained within the monochromator by a mechanical vacuum pump backing a 10 cm Edwards Speedivac oil diffusion pump with a thermo-electrically cooled chevron baffle (Speedivac DCB2B) and a liquid N_2 trap between the diffusion pump and the monochromator.[15] Gratings blazed at 200 and 500 nm having 600 grooves mm^{-1} were used to cover the spectrum; the monochromator linear dispersion with these gratings is 1.6 nm mm^{-1}. Signals from the PMT and the MEM were amplified with a Keithley 417 picoammeter.

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† All concentrations and flow rates in this report are on a volume (number density) basis not on a mass or mass-per-volume basis. For the type of experiments discussed in Section V, where all gases are individually flow metered, the concentration in ppm of a given species, X, mixed with a flow of a carrier gas, Y, then is:
(flow rate of X) × 10^6/(flow rate of X + flow rate of Y).

18. Daniels, F., Williams, J.W., Bender, P., Alberty, R.A. and Cornwell, C.D., Experimental Physical Chemistry, 6th ed., McGraw-Hill, New York, 1962, p. 439.

C. Investigation of Emissions Other than $OH(A^2\Sigma^+ - X^2\Pi)$

A number of spectra covering the 150-600 nm range were taken. Higher wavelengths were not investigated since (i) it is known that in that region O atoms produce the OH Meinel bands with the same spectral distribution and with similar intensities with both C_2H_4 and C_2H_2[19] and (ii) CN emission from N and N/O reactions inside the 600-850 nm region belongs to the same band system (A-X) which emits at shorter wavelengths[20a] and behaves similarly to the (uv/visible) B-X system.[14,21,22]

Most emissions in the 150-600 nm range are far more intense for C_2H_2 than for C_2H_4 and appear unattractive for that reason. The exceptions are the OH(A-X) emission from O-atom reactions (see Section V.D.), the CN(B-X) emissions from N and N/O mixtures and the NO(β,γ) and CO Cameron emissions in the region 200 to 250 nm from N/O mixtures.

1. $CN(B^2\Sigma - X^2\Sigma)$

From our earlier work[14,21,23] it was known that the intensities of the CN(B,A-X) system in N-atom/carbon compound reactions can be enhanced by partially replacing N atoms with O atoms. Moreover, the [O] / ([N] + [O]) ratio which gives the maximum CN intensity differs for different compounds. The latter fact made it attractive to study not only N-atom but N/O reactions as well. The bulk of the experiments were made in the presence of 6 to 12% O_2, an O_2 range representative of that encountered in bag samples if such samples were to be mixed inside a monitor in roughly equal amounts with a $N/O/N_2$ reagent flow. The spectral distributions obtained with C_2H_4 and C_2H_2 are very similar. The most intense emissions

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19. Krieger, B., Malki, M. and Kummler, R., "Chemiluminescent Reactions of Oxygen Atoms with Reactive Hydrocarbons. I. 7000-9000 Å," Env. Sci. Techn. 6, 742-744 (1972).

20. Pearse, R.W.B. and Gaydon, A.G., The Identification of Molecular Spectra, Chapman and Hall, London, 1963, Third ed., (a) p. 111-113. (b) p. 241-242.

21. Fontijn, A., "Mechanism of CN and NH Chemiluminescence in the N-O-C_2H_2 and O-NO-C_2H_2 Reactions," J. Chem. Phys. 43, 1829-1830 (1965).

22. Kiess, N.H. and Broida, H.P., "Emission Spectra from Mixtures of Atomic Nitrogen and Organic Substances," Seventh Symposium (International) on Combustion, Butterworths, London, 1959, p. 207-214.

23. Fontijn, A. and Ellison, R., "Formation of Electronically Excited Species in Nitrogen Atom-Oxygen Atom Reactions Catalyzed by Carbon Compounds. NO ($A^2\Sigma$, $B^2\Pi$) and $O(^1S)$," J. Phys. Chem. 72. 3701-3702 (1968).

are from the B-X,$\Delta v = 0$ transitions; these were studied near 388.3 nm. Under no condition (P = 1 to 7 Torr; bath gas 90%Ar/10% N_2 to 100% N_2; $[O]/([N] + [O])$ ratio variation from 0 to 1) could we observe ratios $I_{C_2H_4}/I_{C_2H_2} \geq 2$ or trends that suggested that larger ratios are obtainable.

It thus appears that on the basis of the selection criteria used here there is little prospect for CN(B,A-X) emission as the basis for reactive hydrocarbon measurements. However, Baity, McClenny and Bell[24] have shown that reasonable agreement can be obtained between CN(B-X) emission measured at 388.3 nm and hydrocarbon reactivity with the exception of C_2H_2. The latter could then be subtracted if an independent C_2H_2 measurement could be devised. Such an approach is less attractive than the OH $\Delta I_{308.9}$ method (Sections V.D and VI) which is not subject to C_2H_2 interference. The CN 388.3 nm emission intensity, moreover, varies strongly with small variations in O_2 content of the sample[24] (factor of 2.4 decrease for an increase of the O_2 conten of the sample from 10 to 20%) and NO_x could also be a major interference because of the rapidity with which it destroys N atoms.[25] In view of the advantages on all these points of the OH $\Delta I_{308.9}$ method we have not further investigated the CN emission.

2. NO(β,γ) and CO Cameron Emissions

Our previous chemiluminescence studies of N/O mixtures had shown that the intensity of the NO β and γ bands, which are characteristic for such mixtures, is slightly enhanced upon addition of C_2H_4, but apparently not upon addition of C_2H_2.[14,23] This phenomenon could best be observed in the 200-250 nm region. More recently we found that C_2H_4, but evidently not C_2H_2, leads to CO Cameron band emission in this wavelength region.[26] These earlier observations were made in an O_2-free system in a study in which C_2F_4 was normally used and C_2H_4 and C_2H_2 were used only incidentally; the observed NOγ light intensities using C_2F_4 were two orders of magnitude higher than with C_2H_4; the Cameron band intensities from C_2F_4 were at least one order of magnitude higher than those from C_2H_4.

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24. Baity, P.W., McClenny, W.A. and Bell, J.P., "Detection of Hydrocarbons by Chemiluminescence with Active Nitrogen," American Chemical Society, Division of Environmental Chemistry, Preprints of Papers 167th National Meeting, Los Angeles, CA, April 1974, p. 310-312.

25. Brocklehurst, B. and Jennings, K.R., "Reactions of Nitrogen Atoms in the Gas Phase," Progress in Reaction Kinetics 4, 1-36 (1967).

26. Johnson, S.E., Fontijn, A. and Miller, W.J., "Kinetics of Vacuum Ultraviolet Chemiluminescence," AeroChem TP-289, AFRPL-TR-73-17, April 1973.

By optimizing conditions (N_2 bath at 1.6 Torr; $\{[O]/([N] + [O])\} = 0.3$; observations near the C_2H_4 inlet nozzle) we succeeded in getting considerable NOY intensity increases (factor of 10) with C_2H_4 and, moreover, found the intensities to be proportional to $[C_2H_4]$ from about 100 to 1000 ppm. O_2 has a definite, but not necessarily prohibitive, quenching effect. However, under these conditions C_2H_2 led to similar increases in intensity. Thus since our goal was to find a method not responsive to C_2H_2 we did not continue this study.

The Cameron bands emission is weakly interspersed between the NOY bands and does not appear practical for hydrocarbon analysis. Since it can be made the dominant spectral feature in the 190-230 nm region when C_2F_4 is used, this emission, as well as the NOY emission, may be useful for chemiluminescence analysis of halocarbons.

D. $OH(A^2\Sigma\text{-}X^2\Pi)$ from O-Atom Reactions

1. Spectral Distribution and Intensities

Figure 2 shows a comparison of the pertinent portion of the $OH(A^2\Sigma\text{-}X^2\Pi)$ system from the O/C_2H_4 and O/C_2H_2 reactions. For both reactants the $(0,0)Q_2$ head at 308.9 nm is a dominant feature; however in the C_2H_4 case it is the dominant feature while for C_2H_2 it is just a dominant feature. Specifically, for C_2H_2 the 312.2 nm $(1,1)R_1$ head has almost the same intensity as the 308.9 nm head, while for C_2H_4 the $(1,1)R_1$ head is very weak. These observations suggest that a measurement of $\Delta I_{308.9} = I_{308.9} - I_{312.2}$ could provide a direct measurement of C_2H_4 in the presence of C_2H_2.† To further investigate this point we measured the spectral distribution of a number of other hydrocarbon species specified by the EPA technical monitor, which are given in Table 1. All of these hydrocarbons (except CH_4 from which no emission could be detected) were found to yield the same spectral distribution as C_2H_4, giving further indications of the

† An alternate choice which might be suitable is to subtract $I_{306.4}$ rather than $I_{312.2}$ from $I_{308.9}$.

suitability of the $\Delta I_{308.9}$ measurement as a measurement method for reactive hydrocarbons free from interference by C_2H_2 and CH_4. The spectra of Fig. 2 were taken at relatively high hydrocarbon concentrations, [HC], to obtain a high light intensity allowing good quality spectral distribution measurements. In further experiments the flow rates of the hydrocarbons of Table 1 were varied over large ranges (by as much as a factor of 40)† and reaction time was varied from 2×10^{-3} to 5×10^{-3} sec. None of these changes produced noticeable changes in spectral distribution, suggesting that the $\Delta I_{308.9}$ method would be valid at all hydrocarbon concentrations of interest. The spectral distribution from O/C_2H_4 also did not change when the pump was throttled to increase the pressure from ≈0.8 Torr at the standard flow conditions (Table 1 and Fig. 3) to 2.0 Torr. This change did however result in a decrease in intensity and further experiments were therefore done at ≈0.8 Torr. The O/C_2H_4 spectral distribution also was found to be the same whether a 6% or 12% O_2 in He bath or a 100% O_2 bath was used. The O/C_2H_2 spectral distribution showed some change with pressure; the intensity of the 'subtract' wavelengths (306.4 and 312.2 nm) decreased somewhat with respect to that at 308.9 nm. Thus we have several reasons for favoring ≈0.8 Torr (near the practical lower limit for a mechanical vacuum pump) to higher pressures. In Section V.D.2 the physico-chemical reasons for some of these observations are discussed.

The next point to establish is the relative response of the individual hydrocarbons other than C_2H_2,‡ at 308.9 nm. Since all hydrocarbons give the same spectral distribution this measurement is the equivalent of a $\Delta I_{308.9}$ measurement. To this end spectra were taken over a range of concentration within the linear part of the response plots (at very high [HC] deviations from linearity occur, cf. e.g. Fig. 3, which can be attributed to

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† In the experiments with the test apparatus, Section VI below, the hydrocarbons were introduced with a flow of air (the counterpart of hydrocarbon diluted in the N_2/O_2 mixture present in bag samples) and the number of ppm (v/v) of hydrocarbon in the sample flow is a meaningful figure, the same as in most air pollutant analyzers. In the experiments of the present section the hydrocarbons flowed directly in the main gas flow and no such definition is possible. The total flow under the conditions of Table 1 contained (before reaction) 1600 ppm of hydrocarbon, corresponding to 4800 ppm in the sample flow under the conditions of Section VI where the reagent flow was twice as large as the sample flow.

‡ The 308.9 nm intensity of C_2H_2 is 0.25 that of C_2H_4, the $\Delta I_{308.9}$ from C_2H_2 is zero by definition (and measurement, cf. Section VI).

TABLE 1. RELATIVE CHEMILUMINESCENCE SIGNAL INTENSITIES OF CLASS V, IV, III, AND I HYDROCARBONS,[a] AT HIGH HYDROCARBON CONCENTRATION IN SURVEY APPARATUS

Class V, Reactivity[a] = 14.3	ΔI_{rel}[b,c]	k[d]
Ethylene	100	4.9×10^{8}
Propylene	104	2.2×10^{9}
Butene-1	91	2.3×10^{9}
Butene-2	94	1.2×10^{10}
Isobutene	78	1.2×10^{10}
Propadiene	48	unavailable
Butadiene	113	1.2×10^{10}
Class IV, Reactivity = 9.7		
Toluene	29	1.4×10^{8}
Class III, Reactivity = 6.5		
n-Butane	6	1.6×10^{7}
n-Heptane	10	7.7×10^{7}
Iso-octane	10	5.5×10^{7}
Class I, Reactivity = 1.0		
Methane[e]	$< 10^{-2}$	$\approx 1 \times 10^{4}$
Ethane	3	5.5×10^{5}
Propane	7	9×10^{6}
Benzene	3	2.4×10^{7}

a Reactivity classes and numbers as suggested by B. Dimitriades.[5]

b Ethylene is taken as 100.

c The observation conditions were the following: Reaction time = 2×10^{-3} sec; P = 0.8 Torr; O_2 flow = 3 ml.atm sec^{-1}; O-atom flow = 4.7×10^{-2} ml.atm sec^{-1}; Hydrocarbon flow = 5×10^{-3} ml.atm sec^{-1}.

d Rate coefficients, in ℓ $mole^{-1} sec^{-1}$, at $\approx 25^{\circ}C$ for the attack of O atoms on the specific hydrocarbon as recommended by Herron and Huie[27] from the available measurements.

e No detectable signals from methane were obtained; the highest methane flow tested was 5×10^{-1} ml.atm sec^{-1}.

27. Herron, J.T. and Huie, R.E., "Rate Constants for the Reactions of Atomic Oxygen (O^3P) with Organic Compounds in the Gas Phase," J. Phys. Chem. Ref. Data 2, 467-518 (1973).

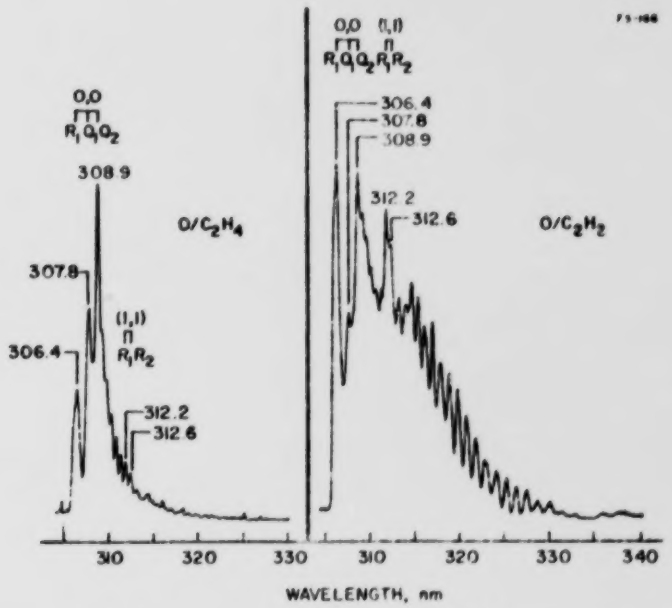

FIGURE 2. $OH(A^2\Sigma\text{-}X^2\Pi)$ emission from the O/C_2H_4 and O/C_2H_2 reaction. The O/C_2H_4 spectrum was obtained at a 3-times more sensitive scale (lower intensity) than the O/C_2H_2 spectrum. Spectrometer bandpass: 0.3 nm; P = 0.8 Torr; O_2 flow 3 ml.atm sec^{-1}; O-atom flow 1.1×10^{-1} ml.atm sec^{-1}; C_2H_4 flow 6.7×10^{-3} ml.atm sec^{-1}; C_2H_2 flow 2.3×10^{-2} ml.atm sec^{-1}.

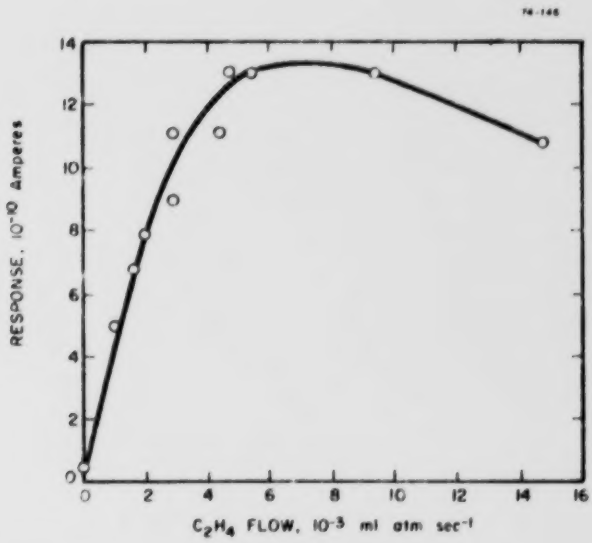

FIGURE 3. $I_{308.9}$ versus C_2H_4 flow. Reaction time = 2×10^{-3}sec; P = 0.7 Torr; He flow 2.2 ml.atm sec^{-1}; O_2 flow 2.4×10^{-1} ml.atm sec^{-1}; O-atom flow not measured, may be estimated as $\approx 1 \times 10^{-2}$ ml.atm sec^{-1}.

the fact that the O-atom consumption is no longer negligible); as can be seen from Fig. 3 such deviations occur at concentrations much higher than are of practical interest, i.e. larger than those corresponding to 1000 ppm. The results of the comparison are given in Table 1. The hydrocarbon flow rate of 5×10^{-3} ml.atm sec^{-1} used fell within the linear range for all the hydrocarbons. The agreement between the intensities obtained and the Dimitriades reactivity ratings[5] is gratifyingly good. On the basis of these observations it was decided to continue with the $\Delta I_{308.9}$ method and to build a test apparatus suitable for a thorough testing of the method at realistic hydrocarbon and potential interference compounds concentrations (see Section VI).

It was further observed, in some additional experiments with the conventional flow tube in which the hydrocarbon nozzle-to-observation window distance was varied, that the strong signals from the Class V compounds decreased with reaction time, while weaker signals from the Class IV, III, and I compounds did not decay within the observed reaction time interval (2×10^{-3} to 5×10^{-3} sec).† It follows that the $\Delta I_{308.9}$ response to the various hydrocarbons can be varied by changing reaction time; this is further confirmed in Section VI.

2. Reaction Kinetics and Kinetic Spectroscopy

The difference in spectral distribution resulting from the C_2H_2 and C_2H_4 reactions with O atoms had been observed previously and is indicative of two different $OH(A^2\Sigma)$ formation reactions leading to formation of rotationally and vibrationally 'hot' and 'cold' $OH(A^2\Sigma)$, respectively.[28] The fact that the other hydrocarbons produce the same spectral distribution as C_2H_4 suggests that the mechanism of $OH(A^2\Sigma)$ formation is the same in all those cases; however this reaction mechanism has not yet been established. The O/C_2H_2 mechanism has been shown to involve O_2 and can probably be attributed to[29]

$$CH + O_2 \rightarrow OH(A^2\Sigma) + CO \qquad (3)$$

† The signals from toluene and n-heptane actually showed a slight increase and those from benzene a strong (factor of 2.5) increase with increasing reaction time.

28. Becker, K.H., Kley, D. and Norstrom, R.J., "OH Chemiluminescence in Hydrocarbon Atom Flames," Twelfth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1969, p. 405-413.

29. Krishnamachari, S.L.N.G. and Broida, H.P., "Effect of Molecular Oxygen on the Emission Spectra of Atomic Oxygen-Acetylene Flames," J. Chem. Phys. 34, 1709-1711 (1961).

While in accord with Reaction (3) the $OH(A^2\Sigma\text{-}X^2\Pi)$ emission from O/C_2H_2 increases initially with O_2 addition, that from O/C_2H_4, etc. only decreases in intensity upon such addition,[30] indicative of $OH(A^2\Sigma)$ quenching by O_2 and of free radical scavenging of an emission precursor by O_2. This difference in O_2 influence on $I_{308.9}$ is illustrated in Fig. 4 for which an N_2/O mixture was used to provide a comparison to an essentially O_2-free situation.† It may be seen that the O/C_2H_2 intensity reaches a maximum and then decreases; this is again indicative of quenching and free radical scavenging effects. Qualitatively similar results to those of Fig. 4a were obtained when propylene, butene-1 or butene-2 was used instead of C_2H_4 and when longer reaction times, higher pressures and $Ar/3\%$ O_2 discharge gas were investigated. For the test/prototype instrument design, these observations indicate $[O_2]$ should be kept relatively low since, at constant $[O]$, $\Delta I_{308.9}$ decreases with increasing $[O_2]$.

The observation (Section V.D.1) that with increasing pressure the O/C_2H_2 spectral distribution becomes more like the O/C_2H_4 distribution is merely evidence for rotational/vibrational relaxation of the relatively long-lived ($\tau_{rad} = 8 \times 10^{-7}$ sec)[31,32] emitter $OH(A^2\Sigma)$ with increasing pressure. Part of the $OH(A^2\Sigma)$ molecules formed will be electronically quenched, i.e. do not contribute to the light emission. Other factors being equal, the fraction of $OH(A^2\Sigma)$ formed that radiates should be kept as high as possible for high sensitivity. To give an idea of this fraction, consider the rate coefficients for electronic quenching, k_q. These are[32] for He, Ar, N_2, and O_2, respectively, $< 6\times10^8$, 6×10^8, 6×10^9 to 3×10^{10}, and $\approx 3\times10^{10}$ ℓ mole^{-1} sec^{-1}. The rate coefficient for light emission k_{rad} equals τ_{rad}^{-1} and the fraction of $OH(A^2\Sigma)$ molecules formed which radiate is $k_{rad}/(k_{rad} + k_q[N_2])$. For 0.5

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† In the present measurements no special O_2 removal traps in the N_2 line were used. Previous observations[29] suggest that in radically O_2-free $N_2/O/C_2H_2$ mixtures the 308.9 nm intensity at 0% added O_2 is much lower than in the case of Fig. 4.

30. Fontijn, A., "Mechanism of Chemiluminescence of Atomic Oxygen-Hydrocarbon Reactions. Formation of the Vaidva Hydrocarbon Flame Band Emitter," J. Chem. Phys. 44, 1702-1707 (1966).

31. Sutherland, R.A. and Anderson, R.A., "Radiative and Predissociative Lifetimes of the $A^2\Sigma^+$ State of OH," J. Chem. Phys. 58, 1226-1234 (1973).

32. Becker, K.H. and Haaks, D., "Measurement of the Natural Lifetimes and Quenching Rate Constants of $OH(^2\Sigma^+, v=0,1)$ and $OD(^2\Sigma^+, v=0,1)$," Z. Naturforsch. 28a, 249-256 (1973).

Torr of N_2 (2.7×10^{-5} mole N_2 per liter) and taking the lower limit to k_q this fraction is $(8 \times 10^{-7})^{-1} / [(8 \times 10^{-7})^{-1} + 6 \times 10^{9} \times 2.7 \times 10^{-5}] = 0.89$. Taking the upper limit to $k_q [N_2]$ or taking 0.5 Torr O_2 we obtain 0.61. Electronic quenching thus is far from negligible even at low pressures.

The rate coefficients for O-atom attack on the hydrocarbons are shown in the last column of Table 1. In general the rate coefficients decreased in the same direction as the photochemical smog reactivity ratings.[5] This appears to be a principal reason that the $\Delta I_{308.9}$ measurements give a reasonably good indication of photochemical smog reactivity (the reactions following the initial O-atom attack are of course also important in determining the light intensity). Because the less reactive hydrocarbons are consumed less rapidly than the more reactive hydrocarbons their intensity will decrease less rapidly with reaction time (distance), which is the reason that temporal/spatial adjustment of the relative $\Delta I_{308.9}$ from the various hydrocarbons is possible (cf. Section V.D.1). The increases in intensity with reaction time observed in e.g. the benzene case, are indicative of the buildup in concentration of a reaction intermediate. The fact that at 2×10^{-3} sec (the observation condition of Table 1) the butenes give a lower reading than C_2H_4 notwithstanding their larger rate coefficient is probably indicative of their faster consumption.

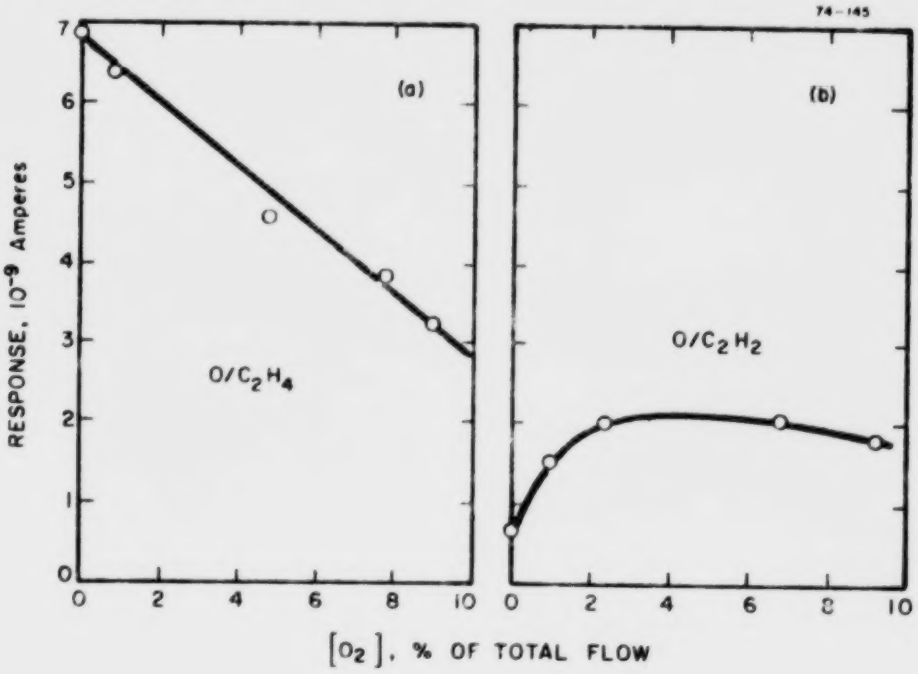

FIGURE 4. Influence of O_2 on 308.9 nm intensities from O/C_2H_4 and O/C_2H_2. Reaction time is 1×10^{-3} sec; P = 1.6 Torr; N_2 flow 11.7 ml.atm sec^{-1}; O-atom flow 9.4×10^{-2} ml.atm sec^{-1}; C_2H_4 and C_2H_2 flows 1.1×10^{-2} ml.atm sec^{-1}.

SECTION VI

THE CHEMILUMINESCENCE HYDROCARBON ANALYZER TEST APPARATUS EXPERIMENTS

The basis for the $\Delta I_{308.9}$ method has been discussed in Section V.D. In order to test the method under realistic bag sample conditions hydrocarbon concentrations of ≈0.1 to ≈100 ppm should be used. This could not be done with the survey apparatus since (i) a spectrometer is not a sufficiently sensitive tool and (ii) regular continuous flow metering devices are not adequate for providing such low concentrations. Another flow tube apparatus (the $\Delta I_{308.9}$ test apparatus) was therefore built, in which (i) interference filters replaced the monochromator, (ii) an exponential dilution flask was used to supply low concentrations of the hydrocarbons, and (iii) a differential electrometer was used to automatically subtract $I_{312.2}$ from $I_{308.9}$.

A. Experimental

1. Gas Handling System and Flow Conditions

The test apparatus is shown in Fig. 5. The O atoms are produced by a 2450 MHz microwave discharge in a 13 mm o.d. Vycor tube. The remainder of the apparatus is made of Pyrex. A 22 mm i.d. Pyrex reaction tube is used. We will refer to the gas passing through the discharge into the reaction tube as the reagent (≡ second reactant) gas. This gas for most of the work was He/9% O_2 (1 ml.atm sec^{-1} He/1 × 10^{-1}ml. atm sec^{-1} O_2). In some experiments 100% O_2 was used to provide a comparison. The He/9% O_2 was chosen for the majority of the experiments since it gives a reasonably high [O], comparable to that available from 100% O_2, yet keeps O_2-quenching at a low level.† The hydrocarbons were introduced through a 2 liter exponential dilution flask using a 0.5 ml.atm sec^{-1} flow of Scientific Grade Air‡ as the carrier gas; the air/hydrocarbon mixture thus simulates the bag sample gas in automotive exhaust monitoring. The average gas velocity down the flow tube under these conditions was 270 cm sec^{-1}. In a few ex-

† With the test apparatus routine [O] measurements could not readily be made. In Section VI.B.4 some relative [O] measurements are discussed. For the work of Sections VI.B. 1-3, the flow conditions and microwave discharge power input were kept constant which resulted in a constant [O], as testified by the reproducibility (±5%) of the $\Delta I_{308.9}$ response with ethylene over the period of these experiments, cf. Section VI.B.2.

‡ This grade air obtained from MG Scientific has the following stated impurities: $NO_x < 5 \times 10^{-3}$ ppm; $CO_2 < 2$ppm; CO ≈ 5 ppm; total hydrocarbons (mainly methane) < 0.1 ppm.

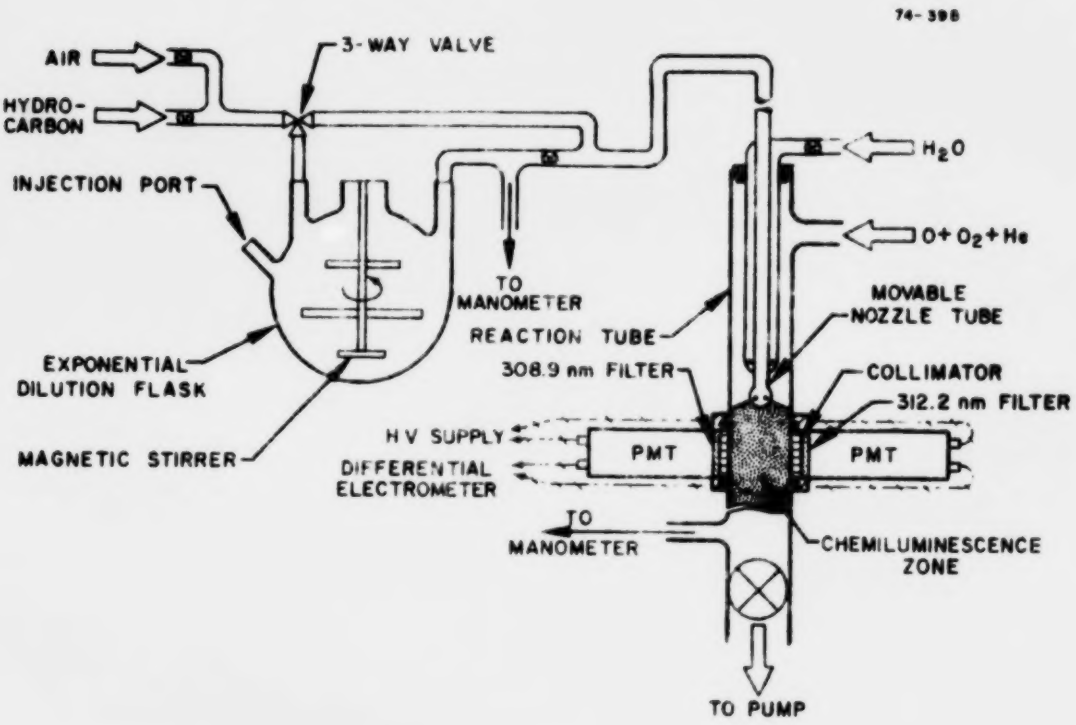

FIGURE 5. The chemiluminescence hydrocarbon analyzer test apparatus.

periments at higher concentrations (≈500-5000 ppm) the HC was also flow metered in directly, bypassing the exponential dilution flask; these experiments served to calibrate the dilution flask output. Gas-tight syringes were used to introduce the hydrocarbons into the dilution flask. Liquid hydrocarbons were injected first into a 5 liter predilution flask and after evaporation and mixing were withdrawn from this flask with a gas syringe for injection into the apparatus dilution flask. Potential interference gases (see Section VI.B.3) were co-injected with the hydrocarbons into the dilution flask. In the case of H_2O it was noticed that the presence of H_2O interfered with the delivery of n-butane. Therefore, in all H_2O interference tests, H_2O was introduced with 0.5 ml.atm sec^{-1} Scientific Grade Air, as shown in Fig. 5, while a constant flow of hydrocarbon, corresponding to 850 ppm in the sample, was used. The pressure in the reaction tube was maintained at 1.2 Torr using a throttling valve in the pump line and a 5 cfm mechanical vacuum pump. All materials were purified as discussed in Section V.B. The exponential dilution flask was kept at 38 Torr, which pressure gave a convenient time decay (≈7 min for a factor 10 decrease in concentration).

The hydrocarbons were dried by passage through silica gel, the remaining reagent and sample gases by passage through activated alumina. Upstream from the microwave discharge and the exponential dilution flasks

the gases passed through liquid N_2 to remove most carbonaceous impurities (except CO, CH_4) that might have been present. To prevent interference from hydrocarbons which might have been present in the flow system, the apparatus was washed with dilute HF before it was put to use. Nonetheless, after several weeks running noticeable increases in the background emission were observed; these were traced to the hydrocarbon inlet nozzle, which was therefore frequently removed and washed with dilute HF. No such repeat cleaning of the rest of the apparatus was found necessary. At the end of the day, the liquid N_2 traps were allowed to warm up and were backpumped; in this way any accumulated impurities were prevented from entering the reaction tube.

2. Radiation Measurement

The chemiluminescence was measured with two matched (approximately equal anode sensitivity, A/lm) Centronic 4242 bialkali PMTs, viewing the reaction zone through a 308.9 and 312.2 nm filter respectively, cf. Fig. 5. The filters were 2.5 cm diam and had a 1 nm half-width with ≥20% peak transmission. Matched PMTs were used to obtain approximately equal intensities at both wavelengths for C_2H_2; electronic gain adjustment allowed the intensities to be made exactly equal. Since the stated wavelength for interference filters is that for perpendicular incidence collimation is required when, as in the present case, a spatially extended glow is observed; the collimators between the reaction tube and the PMTs were 2.5 cm diam, 2.5 cm long (radiator honeycomb) tubes. Since the observation wavelengths are close to the cut-off of Pyrex the transmission of a tube similar to the reaction tube was tested. A clear Pyrex or Vycor tube wall (half cylinder) placed between our present reactor and the monochromator resulted in a 30% decrease in 308.9 nm intensity. (A 50% decrease in intensity was observed when either tube was covered with phosphoric acid.) These losses were considered sufficiently small to retain Pyrex without special windows as the reaction tube material.

3. Electronics

The electronics for the hydrocarbon analyzer basically consist of two current to voltage converters, one for each PMT, and two difference amplifiers whose inputs are the amplified PMT signals. Overload protection for the PMT is also provided.

The light intensity of the chemiluminescent reaction taking place inside the reaction tube, R, Fig. 6 is monitored by PMT1 and PMT2, respectively. The method of amplification of the two PMT signals is the same and consists (for PMT1) of a current to voltage converter, CVC1 (CVC2 for PMT2, etc.), with variable gain selectable on the front panel and two voltage

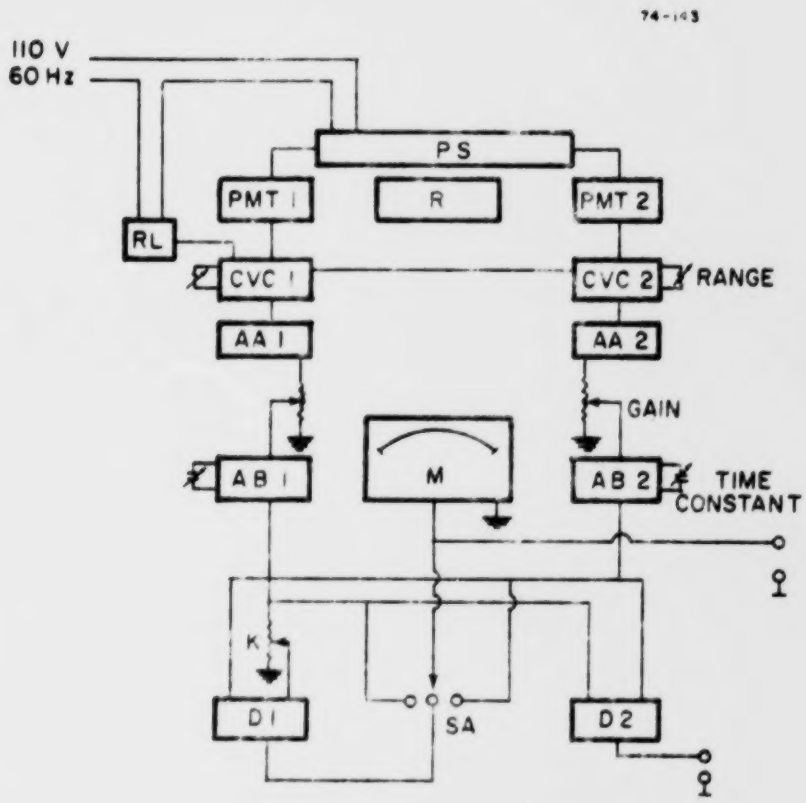

FIGURE 6. Diagram of electronics for the hydrocarbon analyzer test apparatus.

amplifiers, AA1 and AB1, with a gain adjust pot between them. AB1 provides for selection of time constants of 0.3, 1, 3, and 10 seconds with a front panel switch. Also included on each amplifier board (containing CVC, AA and AB) is a current sensor which, when a predetermined anode current on its PMT is exceeded, will shut off the voltage to both PMTs by relay RL. A reset button on the front panel will re-apply power to the high voltage supply when depressed.

The two amplified PMT signals (S_1, S_2) are applied to two difference amplifiers, D_1 and D_2, in such a way as to give KS_1-S_2 and S_2-S_1, respectively, as outputs where K ranges between 0 and 1 and is set on the front panel. K is adjusted to null out the response to C_2H_2 taking into account both the differences in PMT sensitivity and the light intensities at 308.9 and 312.2 nm.

A front panel meter and one set of banana jacks display the amplified outputs of either PMT or the output of D1 (3 position switch SA). Another set of banana jacks provides the output D2, while two more sets of jacks (not shown) make the outputs of AB1 and AB2 available for measurement of $I_{308.9}$ and $I_{312.2}$ individually and for zeroing out dark current and background signal of the respective PMTs. In normal operation the D_1 output corresponding to $\Delta I_{308.9}$ was used. The D_2 output available from S_2-S_1 could be used to measure C_2H_2, which was not done in this work.

B. Results and Discussion

1. Acetylene Zero

A constant flow of C_2H_2 at 8000 ppm was introduced. The relative gain of the two PMT signals was adjusted to give a zero reading of $\Delta I_{308.9}$ under these conditions. If the spectral distribution of O/C_2H_2 does not change when smaller concentrations of C_2H_2 are used, no reading at those concentrations should be obtained either. C_2H_2 from the exponential dilution flask was therefore passed through the zeroed system at concentrations varying from 100 to 1 ppm. No $\Delta I_{308.9}$ signal was received indicating the spectral distribution is independent of concentration, i.e. once the $\Delta I_{308.9}$ instrument is zeroed with C_2H_2 at one concentration it is zeroed at all concentration ranges, which also implies that the spectral distribution from O/C_2H_2 is invariant with $[C_2H_2]$ in this range.

One inherent aspect of the electro-optical arrangement used should be stressed here. The $\Delta I_{308.9}$ output of the instrument is zero for acetylene, once the instrument is zeroed with acetylene. However, the individual PMTs still measure a signal from C_2H_2 at 308.9 and 312.2 nm. As a result one cannot measure concentrations of reactive hydrocarbons in the presence of much larger concentrations of acetylene. Since this situation will not arise in practice, we have not modified the electronics to allow such measurements. The ultimate limitation of course would have been that no reactive HC measurements could be made when their absolute 308.9 nm intensity is comparable to, or less than, the noise in the corresponding C_2H_2 signal.

2. Response to Individual Hydrocarbon Species

To obtain an average Class III reading in roughly the proportion to ethylene indicated by the Dimitriades reactivity table[5] a number of experiments were made in which the nozzle-to-center of observation port distance, i.e. the reaction time, was varied for ethylene and n-butane; the results are shown in Table 2. A distance of 4 cm was selected, corresponding to 1.5×10^{-2} sec, for measurement of all hydrocarbons.

TABLE 2. EFFECT OF NOZZLE DISTANCE ON $\Delta I_{308.9}$ FOR He/9% O_2 DISCHARGE GAS AND 1250 PPM HYDROCARBON

Nozzle-to-Center of Observation Port Distance cm	$\Delta I_{308.9}$ C_2H_4 nA	$\Delta I_{308.9}$ $n\text{-}C_4H_{10}$ nA	Ratio
2	1850	180	10
3	1100	160	7
4	1030	270	4
5	700	320	2

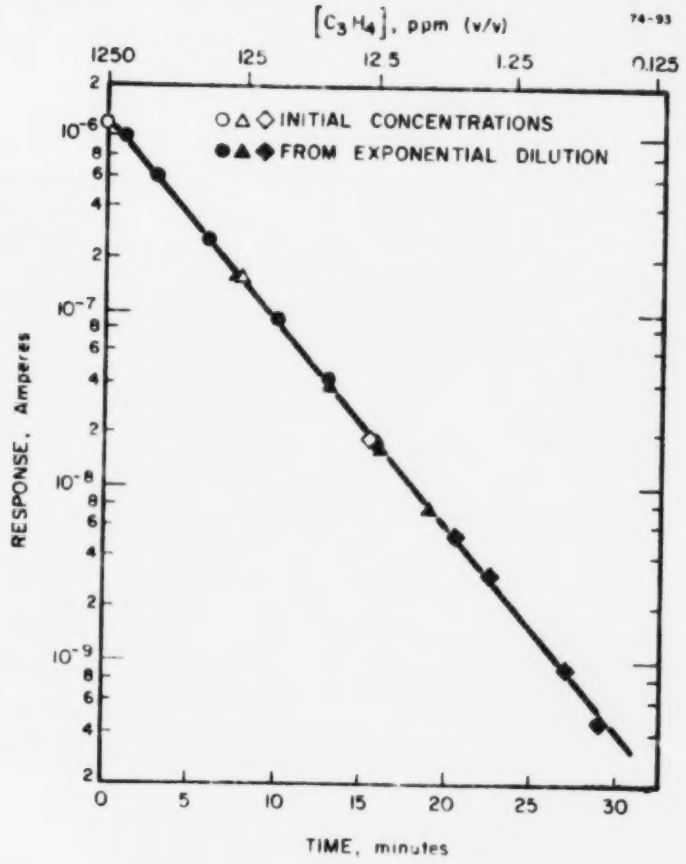

FIGURE 7. Exponential dilution plot for propadiene. Reaction time 1.5×10^{-2} sec; Reaction tube P = 1.2 Torr; Reagent gas flow: He flow 1 ml.atm sec^{-1} / O_2 flow 0.1 ml.atm sec^{-1}; Sample (cylinder air) flow from exponential dilution flask 0.5 ml.atm sec^{-1} with variable hydrocarbon concentration; Exponential dilution flask pressure: 38 Torr.

The relation between signal response and hydrocarbon concentrations had to be established for each hydrocarbon species. This was done by making a number of injections over a wide (typically factor of 100) range of concentrations, cf. e.g. Fig. 7. The points from the exponential dilution plots giving the same response were then assumed to correspond to the same concentrations. Plots of response vs. concentration, e.g. Fig. 8, were prepared from these plots. The response to the individual hydrocarbon species was found to be linear (first power) in their concentration, cf. Figs. 7 and 8 to within a factor of 2 over the full concentration range.

Table 3 compares the $\Delta I_{308.9}$ measurements thus obtained for the individual hydrocarbons. Since the plots are parallel (first order in concentration) any concentration point along the line can be used for this comparison (we used 125 ppm). Because of this linear response the limit of sensitivity, which is ≈0.2 ppm for ethylene, is inversely proportional to the signal response given in Table 3, i.e. ≈1 ppm for n-butane, cf. also Fig. 8.

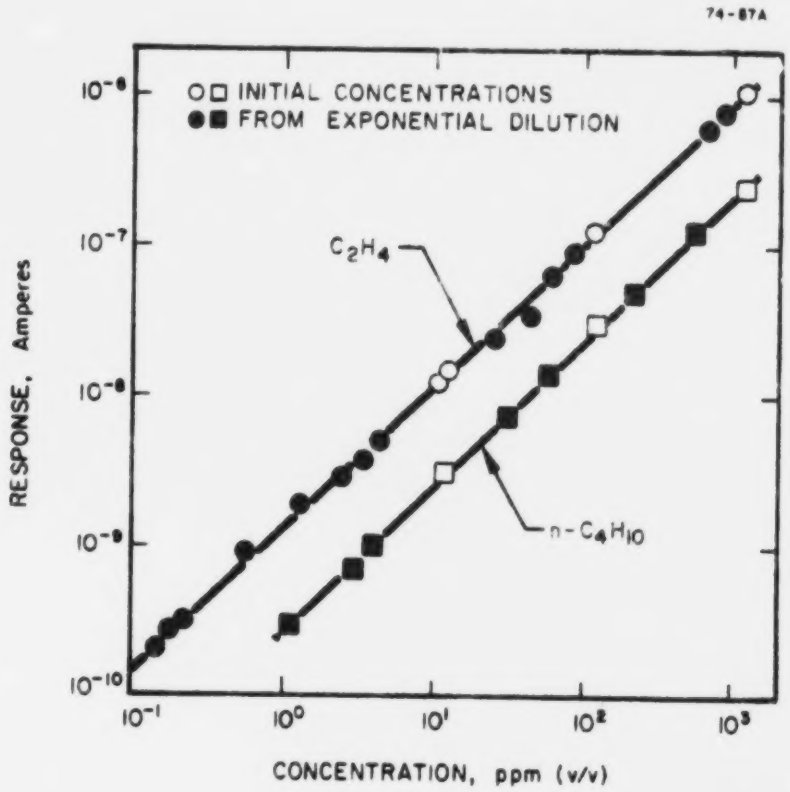

FIGURE 8. Response versus concentration of ethylene and n-butane with He/9% O_2 reagent gas. Conditions as in Figure 7.

TABLE 3. RELATIVE CHEMILUMINESCENCE SIGNAL INTENSITIES OF CLASS V, IV, III, AND I HYDROCARBONS[a] OBTAINED AT 1.5×10^{-2} SEC REACTION TIME FOR He/9% O_2 DISCHARGE GAS

	$\Delta I_{308.9}$[b]
Class V, Reactivity[a] = 14.3	
Ethylene	100
Propylene	42
Butene-1	79
Butene-2	53
Isobutene	38
Propadiene	133
Butadiene	56
Class IV, Reactivity = 9.7	
Toluene	55
Class III, Reactivity = 6.5	
n-Butane	23
n-Heptane	57
Iso-octane	43
Class I, Reactivity = 1.0	
Ethane	1.3
Propane	7.9
Benzene	20
Acetylene[c]	0
Methane[d]	$< 10^{-2}$

[a] Reactivity classes and numbers as suggested by B. Dimitriades.[5]

[b] Ethylene is taken as 100.

[c] The acetylene signals are zero since the instrument is zeroed using acetylene.

[d] No detectable signals from methane were obtained at concentrations up to 1250 ppm, the highest concentration investigated.

In general the $\Delta I_{308.9}$ measurements scale quite satisfactorily with the reactivity factors. Benzene appears to give too high a response and some compounds from Class V too low a response. This should be improvable by decreasing the observation time, cf. Table 2 and Section V.D, but this presumably would lead to a decreased reading for Class III compounds as well. Further control over the relative $\Delta I_{308.9}$ response is possible by varying the [O], cf. Section VI.B.4.

Over a period of several months the response to 125 ppm C_2H_4 was frequently checked. No systematic trends with time were observed and the signal was constant to within $\sigma = \pm 5\%$, about equal to the reproducibility of the data in a consecutive series of tests. This variation is in part due to uncontrollable variation in the amount injected. Test runs on the stability of the light output at a constant hydrocarbon flow showed a maximum ± 3% variation both in short term stability (noise) and long term drift (over a period of 3 days of unattended operation).

3. Interference by Other Species Present in Mobile Engine Exhausts; Influence of Variable % O_2

Other compounds present in exhausts or bag samples could conceivably cause positive or negative interference with the $\Delta I_{308.9}$ hydrocarbon response (positive interference would be emission at the same wavelength, negative interference quenching of the hydrocarbon emission). These effects were investigated by first making a run in which only the interference gas was added to the sample air and then making a run in which the interference gas was added in the presence of the hydrocarbon. Except for H_2O, for which a constant 3% in the sample was used (i.e. the sample was saturated), this was done by injecting the potential interference gas at intervals during an exponential dilution run; typically when the concentration of the interference gas had decreased by a factor of 10 it was re-injected. This is illustrated by Figs. 9 and 10 giving typical recorder traces and an exponential dilution plot derived from such a trace, respectively. It may be seen from Fig. 9 that methane does not interfere with ethylene measurement and does not produce any measurable emission itself, and from Fig. 10 that NO_X does not interfere with n-butane measurement. NO_X was injected into the exponential dilution flask as NO, but in this flask the O_2 of the sample air partially oxidized it to NO_2 thus producing an NO/NO_2 mixture.† Table 4 summarizes the conditions for the interference runs made.

† The same process occurs when the NO from the car exhaust is mixed with the dilution air in the CVS bag sample preparation, i.e. the samples tested are similar in this respect to those with which chemiluminescence hydrocarbon analyzers will be confronted in car exhaust monitoring.

TABLE 4. CONCENTRATION RANGES OF HYDROCARBONS (IN PPM) FOR WHICH INTERFERENCE WAS INVESTIGATED AT THE INDICATED INTERFERENCE GAS CONCENTRATIONS

	CO 1250	CO_2 20,000	H_2O 30,000	SO_2 12.5	C_2H_2 1250-10	CH_4 1250	NO_x 125
Ethylene		850	850		1250-10	6-1	125 -5
n-Butane	125-2	125-2		125-1			1000 -5
Propadiene	1000-0.5	1000-0.5		125-0.5			12.5-0.5
Propane		1000- 10					

74-90A

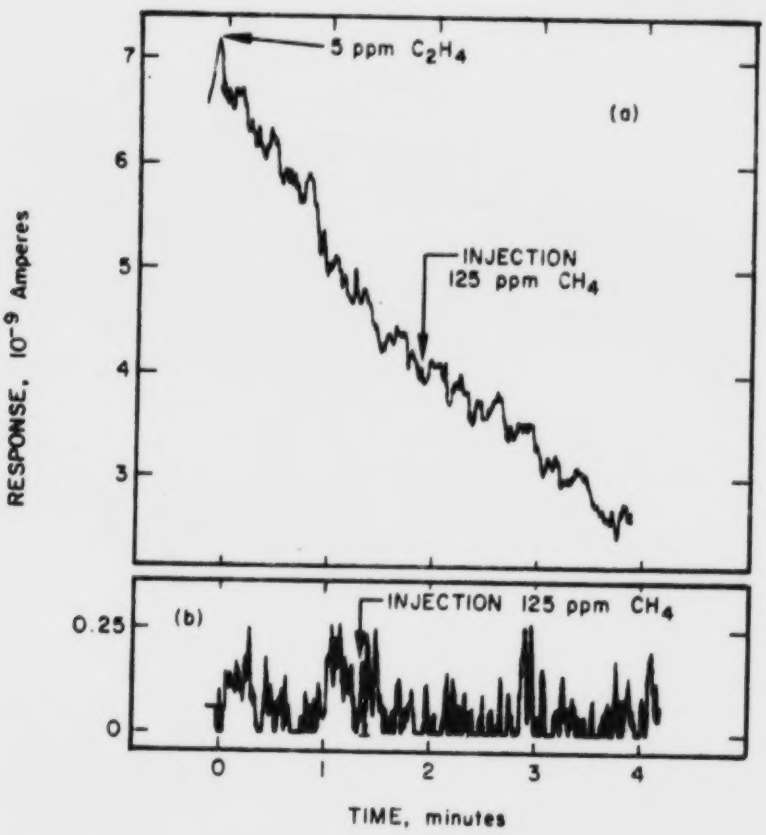

FIGURE 9. Absence of interference by methane. Recorder trace (a) co-injection with C_2H_4, and (b) CH_4 alone. Conditions as in Figure 7.

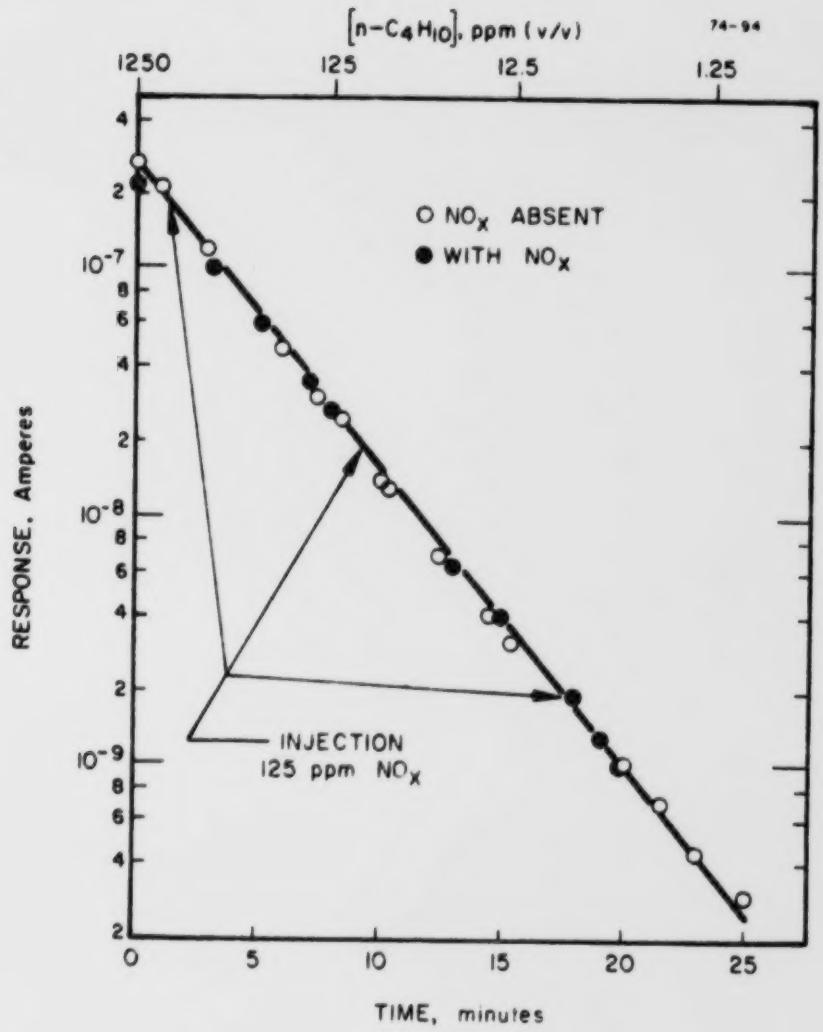

FIGURE 10. Absence of interference of NO_x with n-butane measurement. Exponential dilution plots with and without added NO_x. Conditions as in Figure 7.

No evidence for positive interference was found. The only negative interference occurred with H_2O which caused a 12% decrease in intensity for 850 ppm C_2H_4 (because the interference is only a factor two larger than the variation of consecutive exponential dilution runs, these H_2O measurements were made at a steady C_2H_4 flow after exponential dilution runs suggested that a quenching effect might occur). The interference of the other gases thus was $\leq 5\%$ at the concentrations tested.

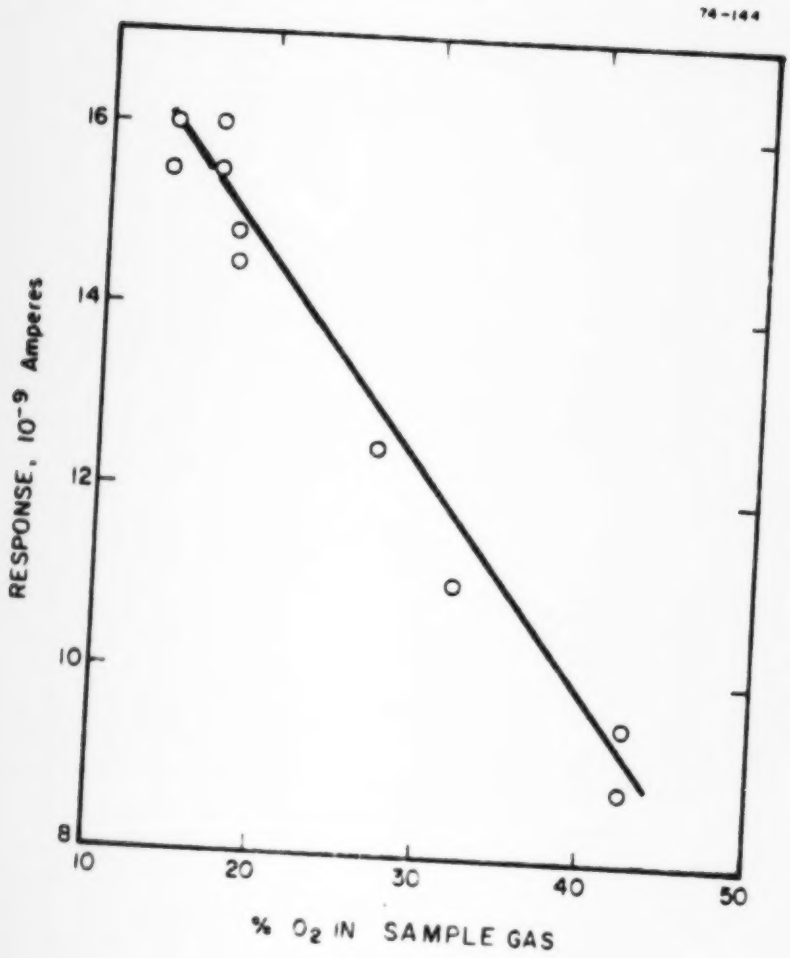

FIGURE 11. Effect of O_2 in sample gas on $\Delta I_{308.9}$ response for 12.5 ppm C_2H_4. Reaction time 1.5×10^{-2} sec; P = 1.2 Torr; Reagent gas (He + O_2) flow 1.1 ml.atm sec^{-1}; Sample gas flow from exponential dilution flask = 0.5 ml.atm sec^{-1}.

Bag samples also will contain a somewhat variable amount of O_2 within the range 15-20%. To investigate the influence of variable O_2, the O_2 content of the sample gas was varied from 14% to 40% (remainder N_2) for 12.5 ppm C_2H_4 injections. This $[O_2]$ range is of course much larger than that of practical interest. The results are shown in Fig. 11. They suggest that a 1% increase or decrease in O_2 content of the sample gases causes somewhat less than about a 1% decrease or increase in the response to ethylene. Thus the effect of normal variations of the O_2 in bag samples is negligible.

4. Measurements with Other Reagent Gas Compositions

Experiments have been made using undiluted O_2 as the reagent gas with ethylene and n-butane sample gas; two different nozzle distances were used under flow conditions otherwise very similar to those used for the He/9% O_2 experiments. The results are shown in Fig. 12. At both distances the response is again first power in [HC]. The C_2H_4/n-C_4H_{10} response ratios at 4 and 2 cm are 14 and 2.5, respectively, similar to those obtained in the He/9% O_2 experiments; however the absolute intensities are a factor of 2 to 3 lower for the undiluted O_2 reagent flow. (Compare Fig. 12 to Fig. 8 and Table 2.) The experiments are not strictly comparable to each other since no attempt was made to keep [O] the same as in the He/O_2 experiments. Experiments in which $[O]_{rel}$ was measured at

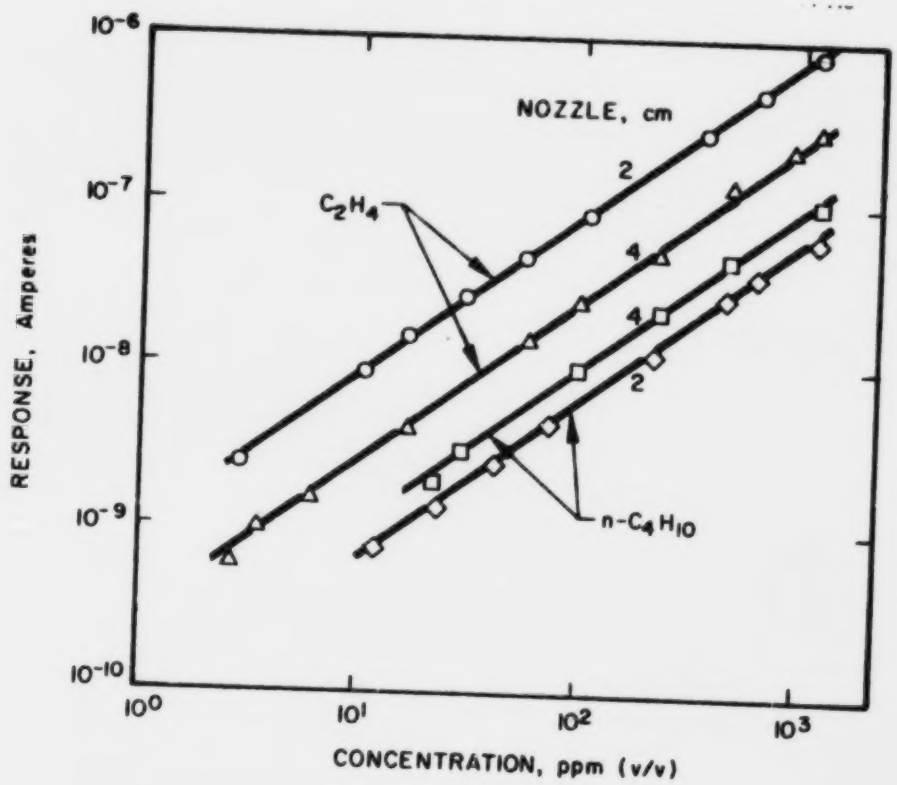

FIGURE 12. Response versus concentration of ethylene and n-butane with undiluted O_2 reagent gas. P = 1.2 Torr; O_2 flow 1.0 ml.atm sec^{-1}; Sample air flow 0.5 ml.atm sec^{-1}.

a number of discharge power levels for the two reagent gas compositions suggest however that [O] was similar for the discussed conditions. Thus this comparison again suggests a quenching effect by O_2, similar to the experiments of Fig. 11 and of Section V.D.

Experiments were next made in He/9% O_2 in which [O] was deliberately varied by a factor of 2 by varying discharge power input. The results are shown in Table 5. It may be seen that decreasing [O] increases the ratio $\Delta I_{308.9}(C_2H_4)/\Delta I_{308.9}(n\text{-}C_4H_{10})$. At 6 cm nozzle distance the absolute response to ethylene also increased. The explanation of these observations is that at lower [O] the ethylene (which has a much higher reaction rate coefficient than n-butane for O-atom attack, cf. Table 1) consumption is decreased and more of it remains to lead to a light producing reaction after longer reaction times. Not enough n-butane consumption occurs on this time scale to observe a similar effect on the absolute $\Delta I_{308.9}$ signal from n-butane. The response under all these conditions is again proportional to [HC].

The conclusion from these experiments is that both nozzle distance and discharge power, i.e. [O], can be used to vary relative $\Delta I_{308.9}$ response of the hydrocarbons in any desired direction.

5. Hydrocarbon Mixtures

Up to now only samples containing one reactive hydrocarbon have been discussed (in Section VI.B.3 it was shown that unreactive hydrocarbons--C_2H_2 and CH_4--do not interfere with the response of reactive hydrocarbons). Bag samples of course contain a mixture of hydrocarbons. To determine whether synergistic effects between reactive hydrocarbons occur, we investigated mixtures of ethylene/n-butane (in a 1:10 concentration ratio) and ethylene/propadiene (in a 1:1 concentration ratio). The results obtained for the ethylene/n-butane mixture are shown in Fig. 13 (those for the ethylene/propadiene mixture spanned a concentration range of 0.5 to 500 ppm). The signals obtained from these mixtures are, within experimental error, equal to the sum of those obtained from the same quantities of the individual compounds. Hence the $\Delta I_{308.9}$ method is apparently not subject to synergistic effects.

TABLE 5. CHANGES IN $\Delta I_{308.9}$ FROM 125 PPM C_2H_4 AND n-C_4H_{10} AS A FUNCTION OF O-ATOM CONCENTRATION FOR He/9% O_2 REAGENT

Nozzle Distance cm	$[O]_{rel}$ [a]	$\Delta I_{308.9}$ (C_2H_4) nA	$\Delta I_{308.9}$ (C_4H_{10}) nA	$\frac{\Delta I_{308.9}\ (C_2H_4)}{\Delta I_{308.9}\ (C_4H_{10})}$
6	2	23	100	0.23
6	1	34	11	3.1
2	2	200	10	20.0
2	1	135	5	27.0

[a] Absolute [O] was not measured. The relative [O] was obtained in a separate experiment in which NO rather than hydrocarbon was passed through the nozzle and the intensity of the emission from the reaction $O + NO \rightarrow NO_2 + h\nu$ was measured. Since[33] $I \propto [O][NO]$ and [NO] was kept constant, a factor of 2 change in light intensity corresponded to a factor of 2 change in [O].

33. Fontijn, A., Meyer, C.B. and Schiff, H.I., "Absolute Quantum Yield Measurements of the NO-O Reaction and Its Use as a Standard for Chemiluminescent Reactions," J. Chem. Phys. 40, 64-70 (1964).

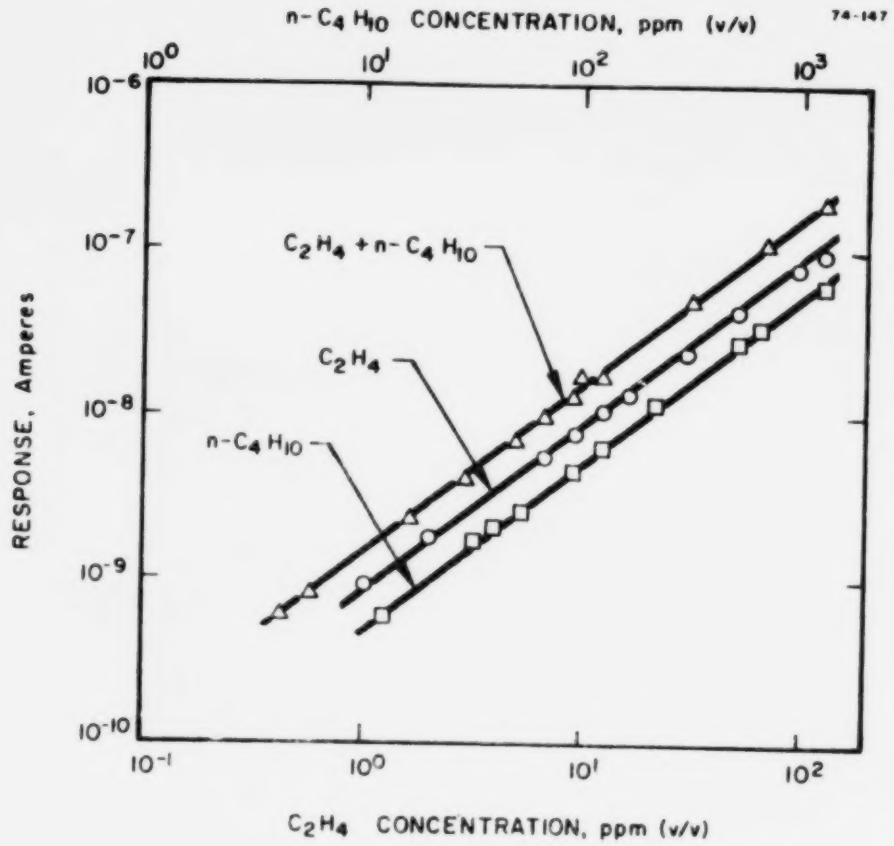

FIGURE 13. Comparison of response of ethylene and n-butane to that of their mixture at the same individual concentrations. The individual points on the C_2H_4 + n-C_4H_{10} line are from the exponential dilution trace of the mixture, the line itself represents the sum of the responses to the individual hydrocarbons as shown in the lower two lines. Conditions as in Figure 7, except for O-atom flow which was not measured.

PART II

MANUAL FOR PROTOTYPE ANALYZER

by

Hermann N. Volltrauer

and

Arthur Fontijn

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SECTION VII

TECHNICAL DESCRIPTION

A. Gas Handling System

1. Sample Gas System

The sample gas is brought into the instrument through a 1/4 in. Gyrolock connector SAMPLE* located on the rear panel (see Fig. 15). From there it flows at a rate of about 1 ml.atm sec^{-1} through a metering valve embedded in a heated aluminum block (to prevent its condensation) to an adjustable inlet nozzle on the reactor. The aluminum block is heated by a 25W cartridge heater (also embedded in the block) which contains a 0.6 cm tube through which the sample flows prior to entering the valve. The block temperature, nominally 120°C, can be adjusted by changing the value of a 75 Ohm resistor wired in series with the heating element and located on a terminal board, TB1, on the side panel above the microwave power supply (see Figs. 16 and 17). Resistors of zero and 100 Ohms result in temperatures of approximately 150 and 110°C, respectively.

2. Reagent Gas System

As discussed in Section X (Tests) below, the 10% O_2 in Ar reagent gas can be used directly from the cylinder, or it can be purified prior to use by a series of traps. In either case the gas is brought into the instrument through a rear panel 1/4 in. Gyrolock connector O_2 at a pressure of 5 to 20 psig. After passing through a normally closed solenoid valve activated by the MAIN POWER switch (which can be overridden by a miniature switch located on terminal boad TB1, Fig. 18), the pressure is reduced to about 1 psig by an internal pressure regulator. The gas then flows either through a toggle valve and metering valve directly into the discharge or first passes through the following series of traps before flowing through these valves and into the discharge:

1. Silica Gel - for removal of water and some hydrocarbons
2. Heated 'Catalyst F' (Engelhard Industries) - operated at about 375°C to oxidize the remaining hydrocarbons and CO to CO_2 and H_2O

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* The terms in capitals refer to the markings on the instrument panels (see Figs. 14 and 15).

FIGURE 11. Front view.

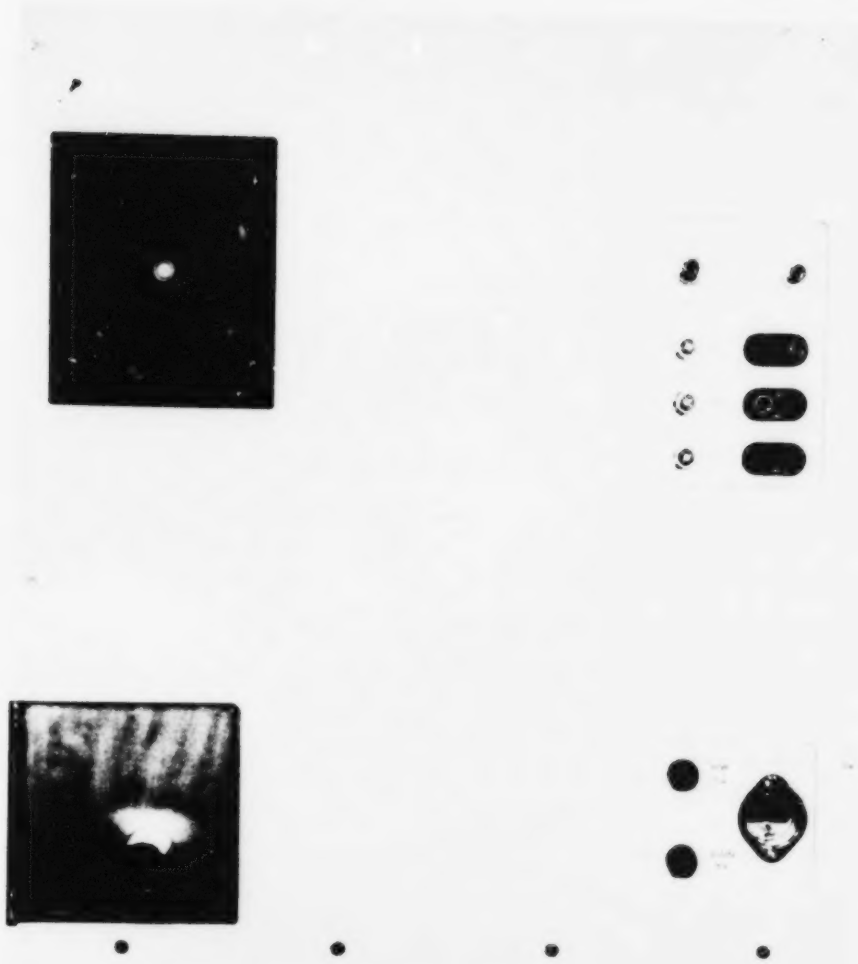

FIGURE 15. Rear view.

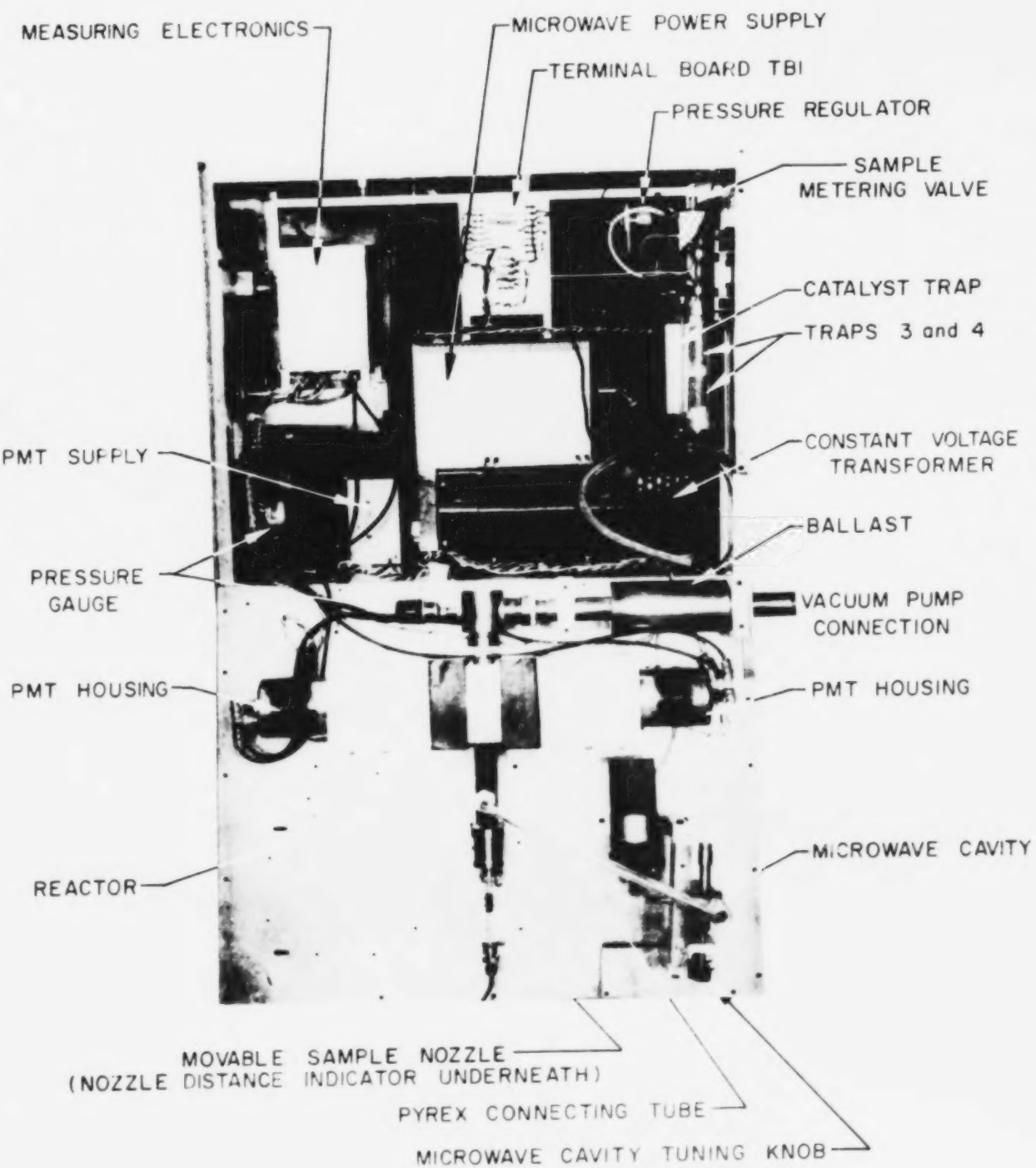

FIGURE 16. View with side panel folded down.

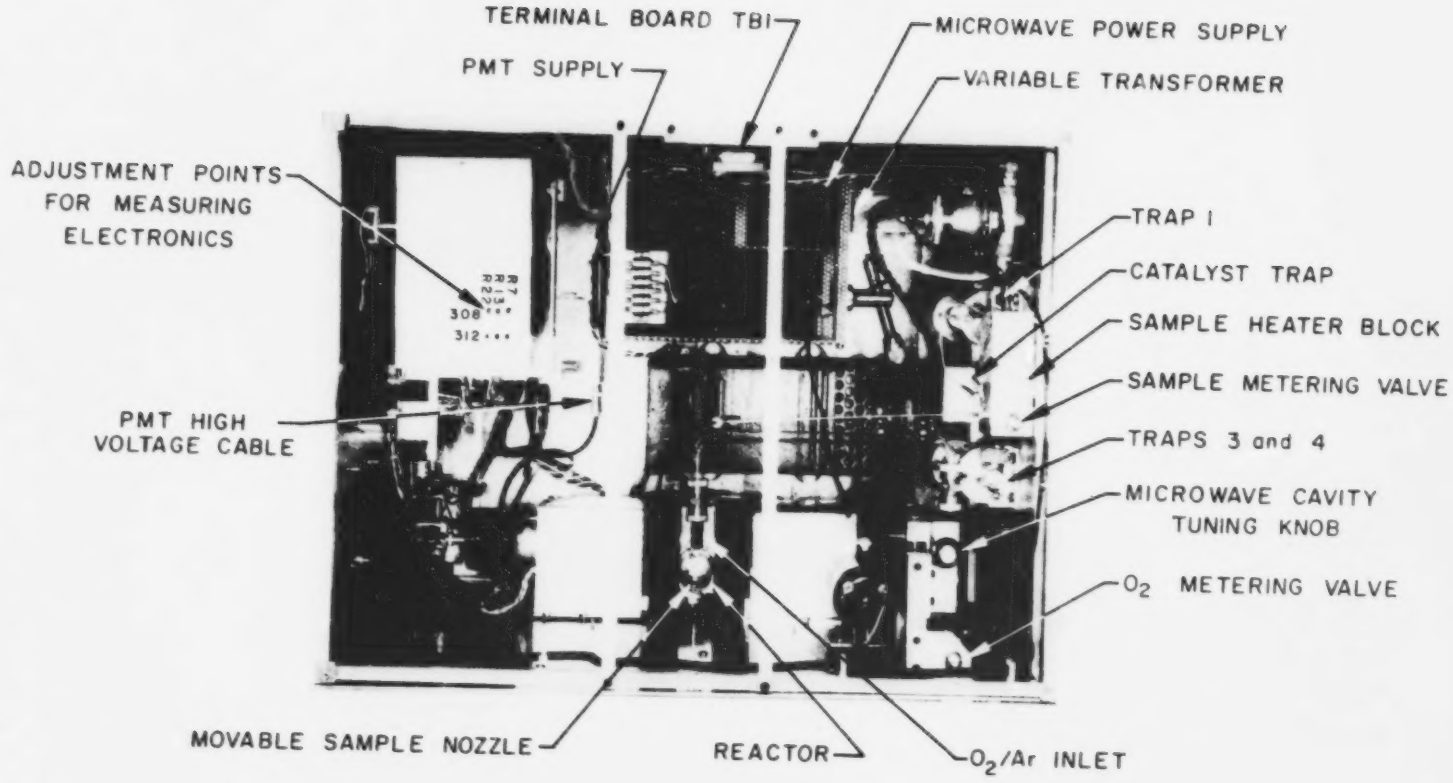

FIGURE 17. Top inside view.

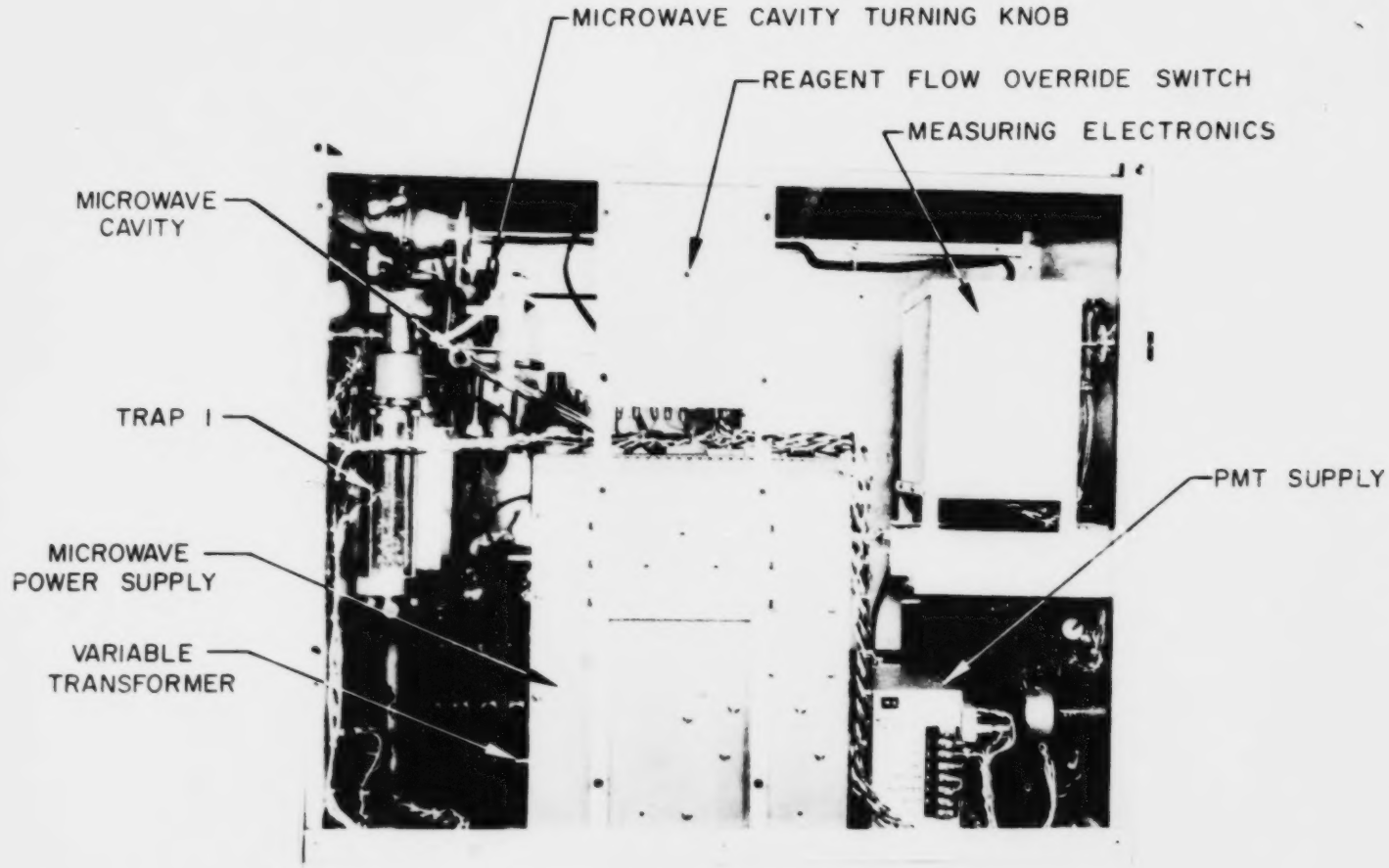

FIGURE 18. Side view with cover off.

3. Silica Gel - for removal of the water produced by 2

4. Ascarite - to remove CO_2

5. Filter - to protect the metering valve and discharge tube

The traps, regulator and filter are located on the rear panel. The first, third and fourth traps are 3.2 cm o.d. Pyrex tubing containing the active materials, while the heated catalyst is inside a 2.5 cm i.d. stainless steel tube wrapped with a 150 W heating element and surrounded by about 2 cm of insulation in an aluminum box. Proper voltage for the heating element for the catalyst trap to operate at about 375°C is obtained by half-wave rectification of the line voltage, but provision for adding a resistor to allow variation of the catalyst temperature is available on terminal board TB1 which also contains the diode used for rectification. Placing a resistor in series or parallel with the diode lowers or raises the temperature of the catalyst, respectively.

With the flow set by the metering valve at about 3 ml.atm sec^{-1}, the gas proceeds through the microwave discharge cavity via a short length of phosphoric acid coated 1.3 cm o.d. Vycor tubing, and then through about 30 cm of 1.2 cm o.d. Pyrex tubing to the reactor, to be mixed with the hydrocarbon-containing sample being analyzed. The Vycor discharge tube, the connecting tube and the reactor are connected with 1/2 in. stainless steel Cajon fittings with Teflon sleeve inserts to prevent destruction of O atoms by the stainless steel.

A 50 cm length of light pipe with one end near the discharge and the other on the front panel DISCHARGE INDICATOR allows monitoring the condition of the discharge. The discharge may also be viewed directly through the fan opening in the rear panel.

3. Reactor and Vacuum Pump

The reactor consists of 2.5 cm o.d. Pyrex tubing 22.9 cm long with a 5 cm long 1.2 cm o.d. side arm 5.1 cm from its inlet end. Cajon fittings at both ends and the side arm facilitate removal of the reactor for cleaning or exchange. The O-atom containing gas enters the reactor through the side arm while the sample gas is introduced through the top of the reactor via a movable 0.6 cm o.d. Pyrex tube. The end of the tube inside the reactor has 8 small holes through which the sample enters the reactor. A 1 to 1/4 in. Cajon adaptor allows easy adjustment of the nozzle distance over a 10 cm range. This distance is indicated by a pointer attached to the tube and can be read from the scale attached to the side panel.

The reactor pressure (which can be used as a quantitative indication of flows) is monitored by a thermocouple pressure gauge (Hastings model VT-4) located at the bottom (downstream end) of the reaction tube in a stainless steel elbow into which the connecting tube (serving as a half liter ballast) for the vacuum pump is fitted.

B. Light Detection System

The reaction is viewed through the Pyrex reactor walls by two matched bialkali PMTs (Centronic type 4242) through narrowband (1 nm) interference filters centered at 308.9 and 312.2 nm. Since the bandpass frequency of the interference filters is dependent on the angle of incidence of the chemiluminescence radiation, collimators (consisting of about 0.3 cm cell size honeycomb) are used between the reactor and filters to insure well-defined transmitted wavelength characteristics of the filters.

C. Electronics

1. Measuring Electronics

The function of the measuring electronics is to (1) amplify the two PMT signals to useable voltage levels and (2) obtain the weighted difference of these voltages and display them on the panel meter and recorder output.

A schematic of the signal processor circuit boards (two are used) is shown in Fig. 19. With the exception of the subtracting circuit which has been added to the 312 board, the two circuits are identical and consist of a current to voltage converter (U1) whose gain is determined by resistors on the ganged (with the corresponding resistors for the 308 circuit to vary both gains simultaneously) range switch. The resistors were chosen to correct from one range to the next for the slight inherent non-linearity of the response of the instrument (see Section X.E) with changes in concentration. This makes the maximum error on any scale due to the non-linearity $\approx 3\%$ of full scale.* Offset current is also fed into U1 to permit zeroing out any background present when zero gas is sampled.

Two ganged potentiometers acting as voltage dividers and accessible on the front panel CALIBRATION are wired between a second (U2) and third (U3) voltage amplifier to allow simultaneous variation of gain of the two circuits for calibration purposes. Front panel selectable TIME CONSTANT, SEC capacitors are included in the feedback circuits of the U3s on a ganged switch

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* A possibly more elegant solution for future instruments might be the use of an operational amplifier programmed to linearize the response.

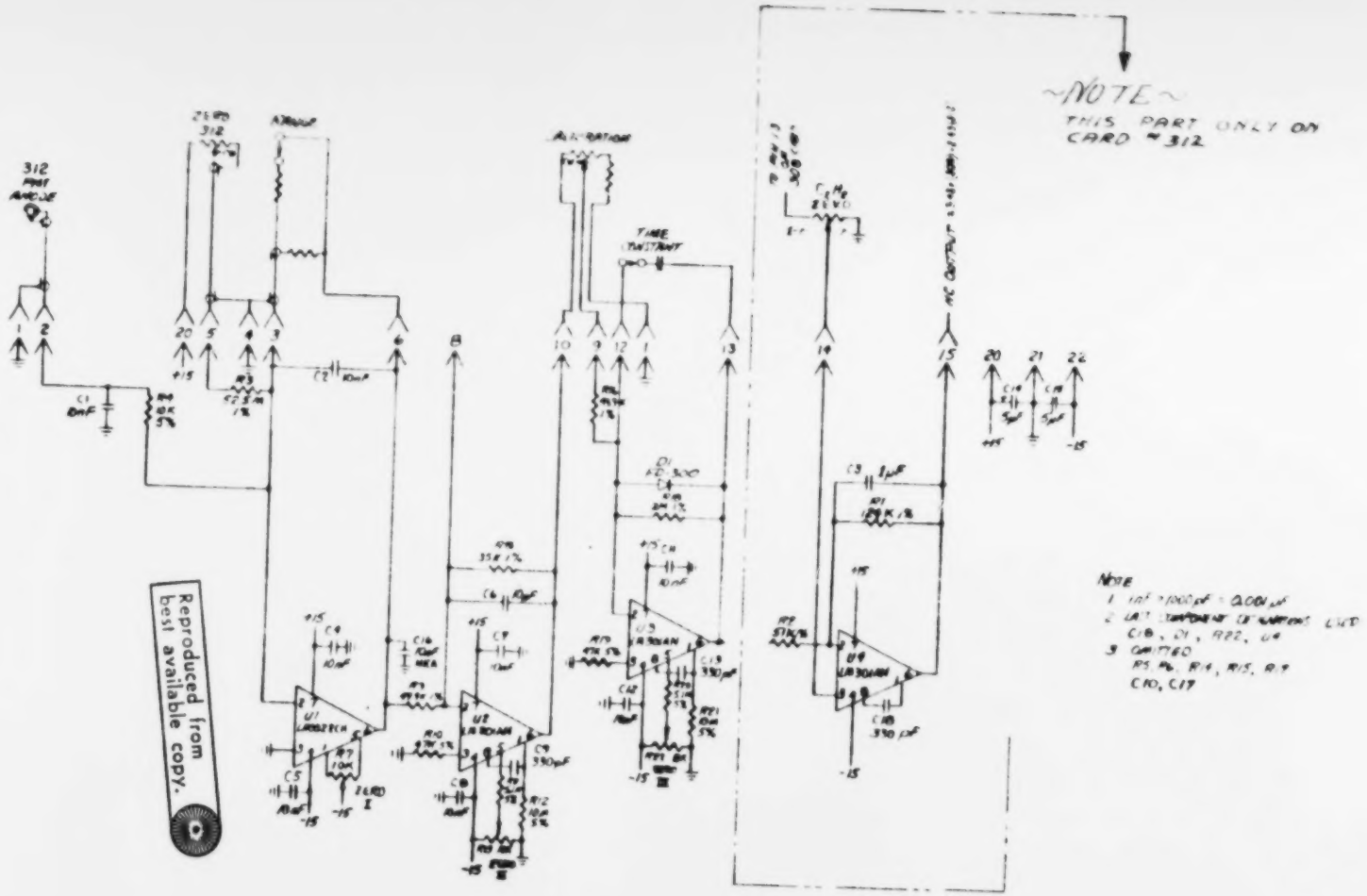

FIGURE 19. Signal processor circuit.

for selection of time constants of 0.1, 0.3, 1, 3 and 10 seconds. The largest range resistor, 50 megohms (which is the one for the 1 ppm range), on each circuit is paralleled with a 0.47 μF capacitor to make the time constant on that range 25 sec.

The 308 output is connected through a 6 V Zener diode to a light emitting diode located on the front panel OVERRANGE which is turned on whenever the voltage across it reaches about 1.5 V. When hydrocarbon concentrations are displayed on the meter this overrange light informs the operator that the signal due to acetylene is greater than the electronics can handle and a higher range should be used. This situation occurs when the 308 signal exceeds about twice full scale.

Subtraction of the 312 from the 308 signal, to obtain a reading corresponding to the hydrocarbon concentration, is performed by U4 on the 312 board. The inverting input of U4 receives the 312 signal to be subtracted directly from U3 through a 50 kilo-Ohm resistor. The gain of U4 to the 308 signal at the non-inverting input is adjusted with the ratio pot on the front panel ZERO C_2H_2 to give zero output with an acetylene sample. The output, HC, of U4 is related to its inputs, (308) and (312) by

$$HC = 2R(308) - (312)$$

where R is the fraction showing on the ZERO C_2H_2 dial (0-1).

Power for driving the operational amplifiers on the two signal processor boards is obtained from a ± 15 V, 220 mA power supply mounted on a third printed circuit board in the electronics enclosure. To prevent high humidity from affecting the performance of the circuits, a higher temperature is maintained inside the electronic enclosure by means of a 1300 Ohm resistor wired to 110 V.

Both PMTs draw their current from a common high voltage power supply located under the electronics enclosure.

2. Microwave Power Supply

Power for the magnetron (Raytheon RK 5609) is supplied by a high voltage (≈ 1500 V) d.c. supply (see Fig. 20) employing a pi section filter to reduce ripple. A variable transformer in the primary circuit is used to control the microwave power, an indication (in % of full scale) of which is obtained on the front panel meter with the MODE switch in the MW PWR position. Access to the Variac transformer dial is obtained on the left side of the instrument with the cover off (see Fig. 18). Regulation for the supply is provided by a 500 VA constant voltage transformer.

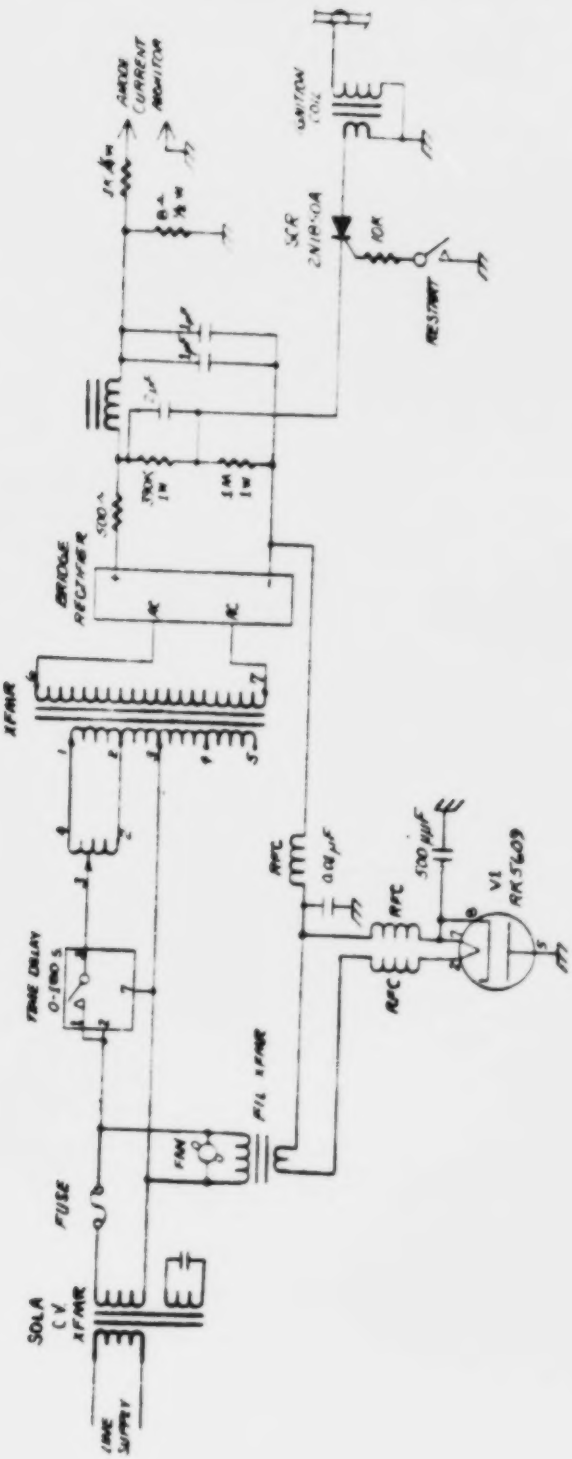

FIGURE 20. Microwave power supply wiring.

Ignition of the microwave discharge is performed by discharging a 0.1 μF capacitor, through the primary of a high voltage transformer (a 6 V automobile ignition coil) by pressing a push button switch DISCHARGE RESTART on the front panel. The secondary of the transformer is placed near the cavity to cause the arc from the transformer to ignite the microwave discharge. The capacitor is charged by a voltage divider connected to the high voltage d.c. of the power supply.

SECTION VIII

OPERATING INSTRUCTIONS

A. Description of Panels and Controls

1. Front Panel (see Fig. 14)

METER	Continuously displays the concentration of the sample being analyzed. The scale is calibrated for 0-1.0 and 0-2.5 parts per million (ppm).
RANGE	Selects the measuring range. There are 8 ranges: 1.0, 2.5, 10, 25, 100, 250, 1000, and 2500 ppm full scale.
TIME CONSTANT SEC	Selects the electronic time constant from 0.1, 0.3, 1, 3, and 10 sec.
ZERO 308, ZERO 312	Provide manual means for balancing out background currents.
CALIBRATION	Provides means to adjust meter reading to a known gas sample concentration.
ZERO C_2H_2	This ratio potentiometer is used to null the instrument response to acetylene.
MODE	Permits displaying one of the following on the front panel meter: 308 signal, 312 signal, hydrocarbon concentration (HC), and relative microwave power in % (MW PWR).
PRESSURE	Monitors pressure in the reactor.
DISCHARGE INDICATOR	Gives indication if discharge is lit (light) or not (dark).
DISCHARGE RESTART	Permits activating the discharge by pressing button.
OVERRANGE	When on indicates that the signal due to acetylene has saturated the 308 electronics

MAIN POWER	Turns instrument on and off.
DISCHARGE POWER	Turns microwave power supply on (only if main power is on) and off.

2. Rear Panel (see Fig. 15)

POWER PLUG	Provides power (110 V a.c. 60 Hz) to the instrument. The main fuse MAIN (8A) and the microwave power supply fuse MW (5A) are located next to the power plug.
RECORDER OUTPUTS	Three double banana plug output jacks supply an adjusted (via the three potentiometers) 0-1 V d.c. output for the 308, 312, and HC signals.
SAMPLE	Provides means for connecting the sample to the instrument.
O_2	Provides means for introducing oxygen to the instrument.
VACUUM	A 2.6 cm o.d. port for connection to an external vacuum pump.

B. Installation and Set-Up

The Pyrex tube connecting the discharge tube to the reactor and the sample inlet nozzle are packed separately for shipment to prevent breakage. They must be re-installed before the instrument is turned on. In addition it is suggested that the following procedure be followed when initially setting up the instrument*:

Step 1. Remove the cover (see Section IX. B. 1).

Step 2. Unpack the Pyrex connecting tube with fittings and Teflon inserts and install (cf. Section IX. B. 4).

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* If other relative reactivity ratings are required see Section X.

Step 3. Unpack and install the sample inlet nozzle (cf. Section IX. B. 3).

Step 4. Connect a 150 l/min vacuum pump to the VACUUM port on rear panel.

Step 5. Connect a source of ≈ 10% O_2 in Ar to the O_2 inlet on rear panel. Pressure should be between 5 and 20 psig.

Step 6. Cap SAMPLE inlet and close toggle valve in O_2 line located near traps on rear panel.

Step 7. Plug instrument power cord and pump power cord into a grounded 110 V, 60 Hz outlet. Turn both on. Press DISCHARGE POWER switch if not lit. The high voltage supply for the magnetron has an automatic three-minute delay from the time the DISCHARGE POWER light has come on.

Step 8. If pressure does not rapidly drop to about 0.1 Torr, find leak and repair.

Step 9. When pressure is ≈ 0.1 Torr uncap SAMPLE inlet and if necessary adjust sample metering valve to obtain a pressure of 0.85 Torr.

Step 10. Open toggle valve in O_2 line and let lines fill with the O_2/inert gas mixture. Adjust pressure to 1.0 Torr with O_2 metering valve. This pressure is correct when Ar is used as inert gas and corresponds to a flow of 3 ml.atm sec^{-1} second reactant.

Step 11. With the MODE switch at MW PWR press DISCHARGE RESTART button. After a few seconds adjust variable transformer (accessible through left side of instrument with cover off, see Fig. 18) for a reading of 20% of full scale.

Step 12. With a hydrocarbon-containing sample connected to the sample inlet and the MODE switch at 308, maximize the meter reading by adjusting the plastic knob on the microwave cavity.

C. Operation

When the installation and set-up have been completed, the instrument should be ready to operate.

If lower concentration samples (50 ppm or less) are to be measured, the background must be zeroed out. It will take from thirty minutes to one hour for the background to reach its minimum value of about 2 ppm equivalent

in the HC mode. To zero out the background connect a zero gas sample to the SAMPLE input and with the MODE switch and the appropriate ZERO knob, alternately display and null the meter for both 308 and 312.

D. Calibration

Complete calibration will involve the measurement of a number of individual hydrocarbons. After the instrument (including the discharge) has been operating for several hours proceed (to obtain a constant background) as follows:

Step 1. With the TIME CONSTANT at 3 sec and the RANGE switch at 2.5 ppm, or higher if necessary, turn the MODE switch to 308 and, using the ZERO 308 knob, null the meter. Turn the MODE switch to 312 and null the meter with the ZERO 312 knob.

Step 2. With the MODE switch at HC and the RANGE at 2500 ppm, introduce an acetylene sample through the rear panel SAMPLE input having a concentration between 10 and 200 ppm. Turn the RANGE switch counterclockwise until the OVERRANGE light comes on, then back off one step. Null the meter with the ZERO C_2H_2 knob.

Step 3. Introduce an ethylene sample of a known concentration between 5 and 500 ppm (with the RANGE switch set accordingly). Adjust the CALIBRATION dial to get agreement between the sample and the meter. If more adjustment than possible with the CALIBRATION dial is needed, turn the CALIBRATION dial to 2 and calibrate using the PMT high voltage adjustment pot, see Fig. 17.

Step 4. Introduce a sample of hydrocarbon (HCX) from a reactivity class other than V (ethylene), e.g. iso-octane, in a known concentration between 50 and 1000 ppm. From the meter reading calculate the ratio of ethylene to HCX response normalized to the same concentration. Using Section X as a guide determine approximate changes in nozzle distance and microwave power needed to obtain the desired ratio for the ethylene to HCX response.

Step 5. With the cover removed (Section IX.B.1) change the nozzle distance by loosening the 1/4 in. Cajon fitting on top of the reactor and gently twist the 0.6 cm Pyrex hydrocarbon inlet tube; bring it to its new location as read on the scale on the side panel. With the MODE switch at the MW PWR position adjust the variable transformer (accessible through the left side of the instrument, see Figs. 17 and 18) until the value determined in Step 4 is obtained.

Step 6. Repeat Steps 3 and 4, and if necessary Step 5, until the desired ratio is obtained.

Step 7. Repeat Steps 1 and 2. This completes the calibration.

An abbreviated (and less accurate) calibration could be carried out by performing only Steps 1, 2, and 3 above or performing Steps 1 and 3 only.

NOTE: Other hydrocarbons can be used for the calibration once enough data is available to relate their responses under varying conditions. Desirable ratios of responses may differ from those suggested here and will depend on the application.

SECTION IX

MAINTENANCE AND TROUBLESHOOTING

A. Planned Maintenance

It is anticipated that only the sample metering valve and some of the Pyrex and Vycor parts will need occasional cleaning. The pressure gauge will give a good indication of the condition of the sample valve, while the sample inlet nozzle is the prime suspect if the background increases.

The only item in the instrument that has a known limited life is the magnetron*; since it is operated well below its maximum current rating, it should have a useful life well in excess of one year. It is important, however, to keep the grid directly above the magnetron clean so as not to obstruct the cooling air circulation.

B. Disassembly and Reassembly

CAUTION: Be sure the MAIN POWER switch is off and the power cord is disconnected before attempting any servicing of the instrument unless explicitly stated otherwise.

1. Cabinet

To gain access to the inside of the instrument, the U-shaped cover must be removed by the following procedure:

Step 1. Remove the 6 screws on the handles.

Step 2. Remove the 7 screws on each side of the cover.

Step 3. Remove the 4 screws holding the fan, lift it out and disconnect it.

Step 4. Lift up the cover.

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* Due to the limited life and long delivery times, we recommend that a spare magnetron (Raytheon RK 5609) be kept on hand.

2. PMT Housing

To replace or service a filter or collimator or to remove a PMT housing for servicing, proceed as follows:

Step 1. With instrument and pump unplugged, remove the cover (Section IX. B. 1).

Step 2. Loosen all four screws visible through the two short horizontal slots in the right (hinged) side panel.

Step 3. Remove the 14 screws around the perimeter of the right side panel but none at the hinge.

Step 4. Disconnect:

(a) the 1/ 4 in. Cajon fitting at the top of the sample inlet nozzle on the reactor,

(b) the 1/8 in. Gyrolock connector (from traps) at the O_2 metering valve,

(c) the microwave cable at the cavity. It may help to tilt the side panel down slightly.

Step 5. Fold down the side panel, after providing support for it.

Step 6. Loosen the 4 screws on the plate holding the two halves of the aluminum reactor block together.

Step 7. Remove the 4 screws for each PMT housing that is to be removed and carefully back up the housing away from the reactor. When free, lift it out. If both housings are to be removed, support for the reactor will be required.

NOTE: Each PMT housing is fitted to its half of the reactor block and to its location on the side panel.

Step 8. After removal place the housing on a clean surface. Remove the 4 plastic screws and pull off the PMT to reactor coupler with collimator. The collimator is press-fitted into the coupler and is easily removed.

Step 9. Remove the plastic spacer and 4 flat head screws. Turn one of the flat head screws partially into a threaded hole of the filter holder and gently pull the filter holder out. This last step exposes the PMT and should be carried out in subdued light.

To reassemble follow above steps in the reverse order being careful in Steps 9 and 8 to properly fit the plastic spacer in the groove. Some twisting of the coupler relative to the housing may be needed in Step 7 to align the PMT housings.

3. Sample Inlet Nozzle

Step 1. With instrument and pump unplugged, remove top panel (see Section IX.B.1).

Step 2. Disconnect the 1/4 in. Cajon fitting at the top of the 0.6 cm sample inlet nozzle tube.

Step 3. Loosen the 1/4 in. Cajon connector at the 1/4 to 1 in. adaptor on top of the reactor and carefully pull out the 0.6 cm tube, twisting it if necessary.

Step 4. Clean the tube by soaking it in dilute (1-5% in H_2O) HF for a few minutes.

CAUTION: HF should not be allowed to come in contact with the skin.

Step 5. Rinse in distilled water and dry.

Step 6. Reassemble.

4. Reactor

Step 1. Follow Steps 1 through 5 of Section IX.B.2 then perform Steps 2 and 3 of IX.B.3 above.

Step 2. Loosen the two 1 in. Cajon fittings at the top and bottom of the reactor. Remove the top one.

Step 3. Loosen both ends of the 1/2 in. Cajon fitting on the side arm.

Step 4. Loosen the 1/2 in. Cajon fitting at the Pyrex elbow end of the discharge cavity.

Step 5. Very carefully lift out the 1.2 cm Pyrex tube containing the bends.

Step 6. Remove the 1/2 in. Cajon fitting at the reactor side arm. Do not lose the Teflon insert.

Step 7. Lift out the reactor and clean as in Steps 4 and 5 of Section IX.B.3, then reassemble.

5. Vycor Discharge Tube

Step 1. Follow Steps 1 through 5 of Section IX. B. 2.

Step 2. Loosen the 1/2 in. Cajon fitting on the side of the bent tube at the side arm of the reactor.

Step 3. Loosen all three connections at the two Cajon fittings at the cavity.

Step 4. Carefully lift out the 1.2 cm bent Pyrex tube.

Step 5. Remove the Vycor tube and clean as in Steps 4 and 5 of Section IX. B. 3 above.

Step 6. Before re-installing this tube coat the inside with phosphoric acid. The recommended method for doing this is to expose some powdery P_2O_5 to the atmosphere and apply the resulting syrupy liquid to the inside of the tube, with e.g. Pyrex wool.

CAUTION: Do not allow the phosphoric acid to come in contact with an organic material; this could result in high background readings.

NOTE: The various parts of the 1/2 in. Cajon fittings are not interchangeable and must therefore be replaced in exactly the same position.

6. Valves

Removal of the O_2 metering valve is straightforward. The only precaution necessary is to avoid excessive pressure on the Vycor tube passing through the cavity.

Access to the heated sample valve is achieved by removing the two screws in the split aluminum heating block and lifting off the top half. Removing the 1/8 in. Gyrolock fitting on the sample inlet line frees the valve and heater assembly which can then be separated by undoing the 1/8 in. Gyrolock connection at the valve. Removing the other 1/8 in. Gyrolock connection frees the valve which can then be opened and cleaned.

7. Microwave Power Supply

Step 1. With instrument unplugged remove top cover (see Section IX. B. 1).

Step 2. Remove microwave cable at supply.

Step 3. Unscrew the wires on the terminal strip on top of the power supply leading away from it. Connections on the terminal strip are from left to right: black, white, orange, yellow, green, black, and blue.

Step 4. Remove the 4 screws on the left side of the instrument holding the supply.

Step 5. Remove the 2 support bars for the fan on top of the instrument and carefully lift out the supply.

C. Troubleshooting

After some initial construction faults were corrected, no problems with the instrument have been experienced at AeroChem, except for the microwave interference which can be easily corrected (see Section IX. D. below). Some possible problems that may arise are the following:

1. Measuring Electronics - if any problems occur that seem to be due to the electronics check the following:

(a) Is the heater in the electronics enclosure operating? (It should be hot to the touch.)

(b) Do the circuit boards fit snugly into their sockets?

(c) Are all cables plugged into PMT bases and into the PMT supply?

(d) Are the fuses good?

If none of the above locates the problem, check for broken wires with the aid of Fig. 21.

2. Meter - If the meter does not read zero with zero air input on the 2500 ppm scale, see Section IX. D.

3. Microwave Power Supply - Operation of the microwave supply can be checked by connecting a UHF diode (IN23) to a milliammeter and holding the diode near the cavity. Zero current indicates the absence of microwave radiation. The most likely source of this problem would be the magnetron, followed by the high voltage power supply (see Fig. 20).

4. Light Leaks - These should be no problem because of the small bandwidth of the filters used. If tests indicate the contrary (more than 1 ppm equivalent signal at 308 or 312 in a normally lit room with the cover off and the microwave supply off) it is likely that a filter has become displaced (see Section IX. B. 2).

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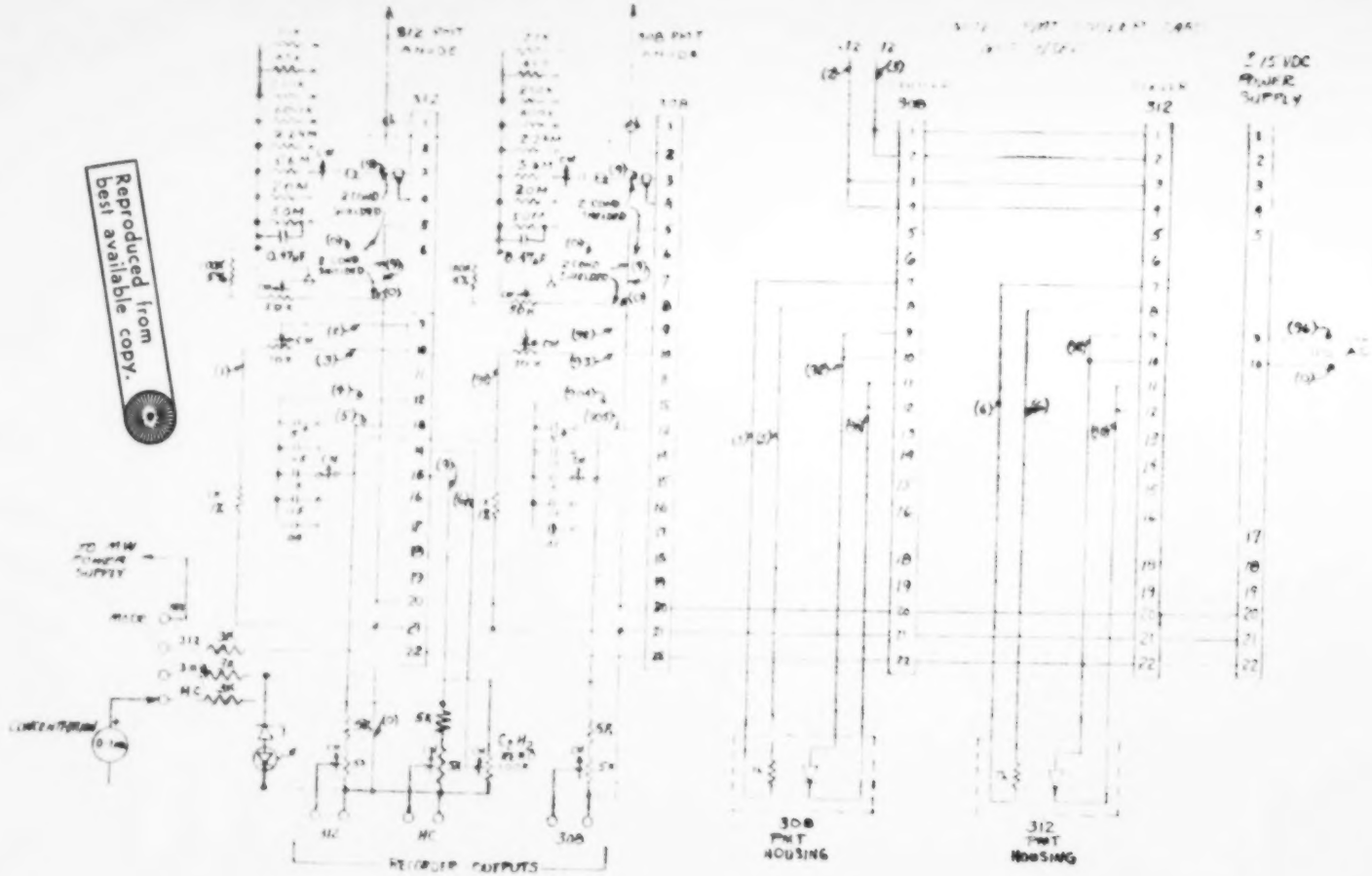

FIGURE 21. Chassis wiring.

5. Air Leaks - With both metering valves off, the pressure gauge should read less than 0.1 Torr. Higher readings indicate a leak, a faulty valve or a faulty pump. Leaks can be easily pinpointed by spraying acetone on suspected joints and watching for pressure increases.

D. Signal Processor Board Adjustments

Due to a small microwave radiation induced electrical interference, the signal may be affected by changes in the microwave power level. This interference can easily be zeroed out with the voltage offsets of the operational amplifiers. When changes in microwave power are made the output of the instrument should be checked on the 2500 ppm scale by sampling ambient air. If the output is not zero, the following alignment procedure should be followed.

Step 1. Note reading on CALIBRATION dial (it will be used in Step 15).

Step 2. Unplug analyzer from the 110 V supply.

Step 3. Remove the cover (see Section IX.B.1).

Step 4. Unplug PMT high voltage cable at the power supply, see Fig. 17.

Step 5. Plug in unit and depress MAIN POWER switch. (Depress DISCHARGE POWER also if this button is not lit.) Wait until meter reads magnetron anode current (i.e. with the MODE switch at MW PWR position a positive reading should be obtained) and depress DISCHARGE RESTART button a few times until discharge lights.

Step 6. Turn both (308 and 312) ZERO knobs fully clockwise.

Step 7. With MODE switch at 312 and CALIBRATION knob at 10 (fully clockwise) adjust R7 (R7, R13 and R22 are the adjustment points for the measuring electronics, see Fig. 17) of the 312 card so that the same positive meter reading is obtained on the 1 and 2500 ppm range. R13 may have to be adjusted to get a positive reading.

Step 8. Reduce reading to $\approx 5\%$ of full scale with R13 and note exact reading.

Step 9. Turn CALIBRATION to zero and note reading. If meter is below zero bring up with R22, then obtain readings with CALIBRATION at 10 and 0.

Step 10. Adjust R13 to make reading with CALIBRATION at zero 10% less than the difference in readings between CALIBRATION at 10 and zero, e.g. if reading is 17 and 5 for CALIBRATION settings of 10 and 0 respectively adjust, while at 0, for 5-0.1(17-5) = 3.8.

Step 11 Repeat Step 10 until the same reading is obtained at both extremes of the CALIBRATION pot (e.g. 10 and 0).

Step 12 Null the meter with R22.

Step 13 Repeat Steps 7 through 11 with MODE switch at 308 and operating on 308 card.

Step 14. Turn MODE switch to HC and zero meter using R22 of 308 card.

Step 15. Return CALIBRATION dial to original setting obtained in Step 1.

For any one CALIBRATION setting the adjustment can be simplified as follows. Perform Steps 2, 3 and 5 of above. Then while sampling ambient air on the 2500 RANGE of 312 adjust R22 (also R13 if necessary) of the 312 card to null the meter. Turn the MODE switch to HC and adjust R22 (also R13 if necessary) of the 308 card to again null the meter. If the meter reading can be made zero with the ZERO knobs at both 308 and 312 MODE settings on the 1 ppm scale, the instrument is zeroed on all ranges.

E. Shipping

Should it become necessary to ship the instrument, please observe the following:

Step 1. Remove all external connections.

Step 2. Remove and pack separately the Pyrex connecting tube and the 6.4 cm hydrocarbon inlet tube (see Sections VIII. B and IX. B).

Step 3. Use the original shipping container or another suitable container and surround the instrument by at least 10 cm of packing material.

SECTION X

TESTS

The instrument was subjected to a number of tests to (i) check its general performance, (ii) select conditions that result in a satisfactory agreement with the Dimitriades scale and at the same time lead to high sensitivity and (iii) determine the linearity and sensitivity of the instrument at those conditions.

A. Reagent Gas Purification Traps

The instrument was found to operate satisfactorily when the traps in the reagent gas line were bypassed; we therefore performed all further tests in that mode. However the traps have been included with the instrument for possible use under special operating conditions e.g. when O_2/He reagent gas, which may contain hydrocarbons, is used. They may also provide zero air.

B. Collimators

A number of lengths of 0.3 cm cell-size honeycomb were used in front of each PMT and the signal-to-noise ratio was measured for ethylene (after zeroing for acetylene). The differences in signal-to-noise ratios were small; the best ratio was achieved when the 308 collimator was 2.5 cm long and the 312 collimator was 1.3 cm long.

C. Flow Rates

A reagent flow rate of ≈ 5 ml.atm sec^{-1} with a sample flow of ≈ 1 ml.atm sec^{-1} gave satisfactory agreement with the Dimitriades ratings[5] (Sections X.D and F) and resulted in a sensitivity of 0.05 ppm ethylene equivalent. These flow rates result in a reading of 1.6 Torr on the front panel pressure gauge and were used for all further tests. Increased sample flow may result in an increased sensitivity; however as a result of such increases, the linearity will suffer at the upper limit (near 2500 ppm) and response ratios will change. Any choice of flow rates is to a large extent arbitrary and other considerations may dictate flow rates different from those chosen.

D. Nozzle Distance and Microwave Power

Under the flow conditions of Section X.C the response of the instrument to ethylene, iso-octane and benzene* was determined as a function of nozzle-to-center of observation port distance and microwave power level (as % of full scale; 100% = 125 mA anode current), see Fig. 22.

E. Linearity and Limit-of-Sensitivity

At 20% microwave power detailed data were obtained for ethylene and limited (over 1 or 2 orders of magnitude) data for some other hydrocarbons. The lowest detectable ethylene concentration (S/N = 2) was found to be ≈ 0.05 ppm. In these tests known amounts of hydrocarbons were introduced with air into a 5 liter exponential dilution flask. To calibrate the dilution flask concentration of NO versus time was measured with an AeroChem Model AA-5 commercial chemiluminescence NO monitor which has a known linear response. The signal of the hydrocarbon analyzer was initially found to be proportional to $[\text{hydrocarbon concentration}]^{0.96}$. This dependence would result in a 7% deviation from linearity per decade. A similar slight deviation had been suggested by the test apparatus results. In the instrument delivered to EPA this deviation is corrected electronically, cf. Section VII.C.1.

F. Response Ratios

The response of some other hydrocarbons relative to that of ethylene for a given concentration of each is presented in Table 6 for a nozzle-to-center of observation port distance of 1 cm and 20% and 30% microwave power levels. The 5 liter exponential dilution flask (Section X.E) was again used in these tests.

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* Benzene was used since it is the Class I hydrocarbon most likely, cf. Table 3, to give too high a reading and therefore required closest scrutiny.

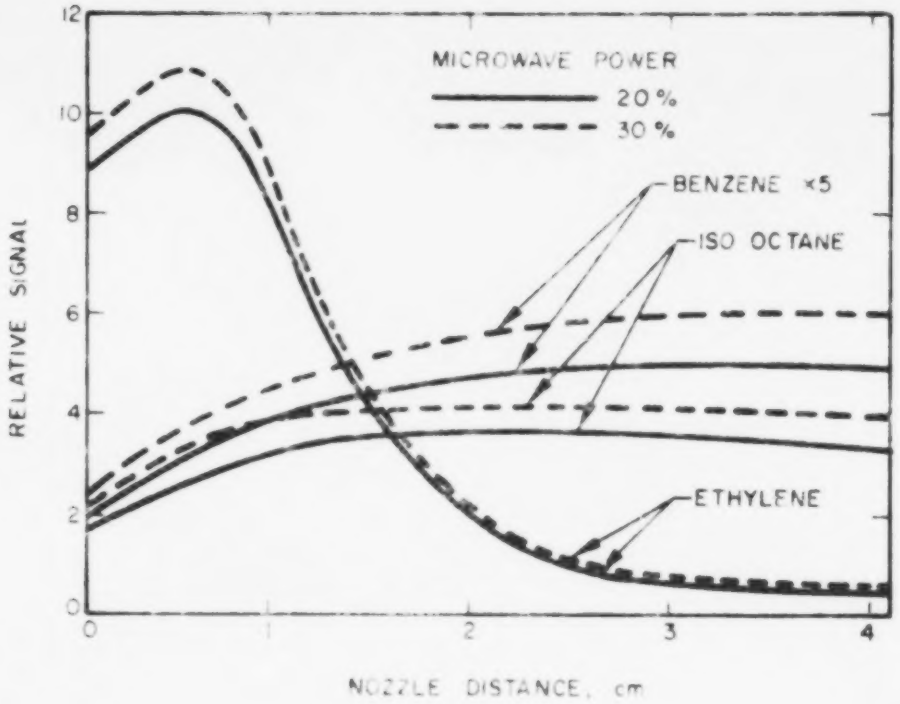

FIGURE 22. Response for ethylene, benzene and iso-octane as a function of nozzle-to-center of observation port distance and microwave power. Sample flow 1 ml. atm sec^{-1}; Reagent (10% O_2/Ar) flow 5 ml. atm sec^{-1}; P = 1.6 Torr.

TABLE 6. PROTOTYPE ANALYZER RELATIVE CHEMILUMINESCENCE SIGNAL INTENSITIES OF CLASS V, IV, III, AND I HYDROCARBONS[a] AT MICROWAVE POWER LEVELS OF 20% (A) AND 30% (B) OF FULL SCALE

Class V. Reactivity[a] = 14.5	A	B
Ethylene	100	100
Propylene	82	77
Butene-1	96	91
Isobutene	70	71
Class IV. Reactivity = 9.7		
Toluene	40	42
Class III. Reactivity = 6.5		
n-Butane	14	18
Iso-octane	47	54
Class I. Reactivity = 1.0		
Propane	7.3	8.0
Benzene	8.6	9.8
Acetylene	0	0

[a]Reactivity classes and numbers as suggested by Dimitriades.[5]

[b]Operating conditions: Nozzle-to-center of observation port distance, 1 cm; Sample flow, 1 ml.atm sec^{-1}; Reagent (O_2/ 10% Ar) flow 3 ml.atm sec^{-1}; P = 1.6 Torr.

SECTION XI

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SECTION XII

INVENTIONS AND PUBLICATIONS

A patent application entitled "Chemiluminescent Method and Apparatus for Determining the Photochemical Reactivity of Organic Pollutants in a Gaseous Mixtures" by Arthur Fontijn was filed by EPA on February 10, 1975; serial number 548471.

A paper was submitted to Environmental Science and Technology on April 14, 1975. It is entitled "Homogeneous Gas-Phase Chemiluminescence Measurement of Reactive Hydrocarbon Air Pollutants By Reaction with Oxygen Atoms" by Arthur Fontijn and Roy Ellison.

APPENDIX A: LIST OF MANUFACTURERS OF PARTS USED IN PROTOTYPE INSTRUMENT

AeroChem Research Laboratories, Inc. Princeton, NJ 08540	Signal Processor Boards AeroChem D-28
	PMT Housing AeroChem G-1
API Instruments Co. Chesterland, OH 44026	Panel Meter API603 0-1 mA DC
Automatic Switch Co. (ASCO) Florham Park, NJ 07932	Solenoid Valves Asco 8262C 35 VM
Bailey Instruments Co. Saddle Brook, NJ 07662	PM Is Centronic 4242
Bertan Associates, Inc. Hicksville, NY 11801	PMT Power Supply Bertan Model 602
Conoflow Corp. Blackwood, NJ 08012	Low Pressure Regulators Conoflow H 10XT 1014 05
Corion Instrument Corp. Waltham, MA 02154	Interference Filters 308.9 nm and 312.2 nm (both 1 nm FWHM, ≥ 20% peak transmission and 2.5 cm diam)
Hastings-Raydist Co. Hampton, VA 23361	Vacuum Gauge Hastings VT4 with DV40 tube
Raytheon Service Company Newton Upper Falls, MA 02164	Magnetron Raytheon RK 5609
Scintillonics, Inc. Fort Collins, CO 80521	Microwave Supply Components Scintillonics Model HV-15A